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Studies on Application of Silyl Groups in Ring-Closing Metathesis Reactions and Fragment-Based Probe Discovery

Abstract

In efforts to search for tool compounds that are capable of probing normal and disease-associated biological processes, both quality and identity of the screening collection are very important. Towards this goal, diversity-oriented synthesis (DOS) has been explored for a decade, which aims to populate the chemical space with diverse sets of small molecules distinct from the traditional ones obtained via combinatorial chemistry.

In the practice of DOS, macrocyclic ring-closing metathesis (RCM) reactions have been widely used. However, the prediction and control of stereoselectivity of the reaction is often challenging; chemical transformation of the olefin moiety within the product is in general limited. Chapter **I** of this thesis describes a methodology that addresses both problems simultaneously and thus extends the utility of the RCM reactions.

By installing a silyl group at the internal position of one of the olefin termini, the RCM reaction could proceed with high stereoselectivity to afford the (*E*)-alkenylsiloxane regardless of the intrinsic selectivity of the substrate. The resulting alkenylsiloxane can be transformed to a variety of functionalities in a regiospecific fashion. The conversion of the (*E*)-alkenylsiloxanes to alkenyl bromides could proceed with inversion of stereochemistry for some substrates allowing the selective access of both the *E*- and *Z*-trisubstituted macrocyclic alkenes. It was also found that the silyl group could trap the desired mono-cyclized product by suppressing nonproductive pathways.

Chapter **II** of this thesis describes the application of the concept of DOS in the area of fragment-based drug discovery. Most fragment libraries used to date have been limited to aromatic heterocycles with an underrepresentation of chiral, enantiopure, sp^3-rich compounds. In order to create a more diverse fragment collection, the build/couple/pair algorithm was adopted. Starting from proline derivatives, a series of bicyclic compounds were obtained with complete sets of stereoisomers and high sp^3 ratio. Efforts are also described toward the generation of diverse fragments using methodology described in Chapter **I**. The glycogen synthase kinase (GSK3β) was selected as the proof-of-concept target for screening the DOS fragments.

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Abbreviation

ADP	adenosine diphosphate
ATP	adenosine triphosphate
B/C/P	build couple pair
bHLH	basic helix-loop-helix
Boc	*tert*-butoxycarbonyl
CM	cross metathesis
CyP450	cytochrome P450
DCM	dichloromethane
DIPEA	*N,N*-diisopropylethylamine
DMEDA	*N,N'*-dimethylethylenediamine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DOS	diversity-oriented synthesis
DPPF	1,1'-bis(diphenylphosphino)ferrocene
EA	ethyl acetate
EDC	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide
FBDD	fragment-based drug discovery
Grubbs I (G-I)	Grubbs catalyst first generation
Grubbs II (G-II)	Grubbs catalyst second generation
GSK	glycogen synthase kinase
HDAC	histone deacetylase

HEPES	4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
HFIP	hexafluoroisopropanol
Hoveyda-Grubbs I (HG-I)	Hoveyda-Grubbs catalyst first generation
Hoveyda-Grubbs II (HG-II)	Hoveyda-Grubbs catalyst second generation
HTS	high-throughput screening
IR	infrared
ITC	isothermal titration calorimetry
LC-MS	liquid chromotography-mass spectrometry
NIS	*n*-iodosuccinimide
NMR	nuclear magnetic resonance
NOE	nuclear overhauser effect
Nosyl (Ns)	2-nitrophenylsulfonyl
PTFE	polytetrafluoroethylene
RCAM	ring-closing alkyne metathesis
RCM	ring-closing metathesis
SAR	structure-activity relationship
SFC	supercritical fluid chromatography
SPR	surface plasmon resonance
SSAR	stereochemical structure-activity relationship
STD	saturation transfer difference
T.brucei	*Trypanosoma brucei*
TBAF	tetra-*n*-butylammonium fluoride
TBS	*tert*-butyldimethylsilyl

TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromotography
TMS	trimethylsilyl
TMSOTf	trimethylsilyl triflate
TS	transition state
Ts	*p*-toluenesulfonyl
WaterLOGSY	water ligand optimized gradient spectroscopy

Chapter I.

Extending the Utility of Ring-Closing Metathesis Reactions through the Introduction of a Silyl Group

Chapter I-1. Introduction

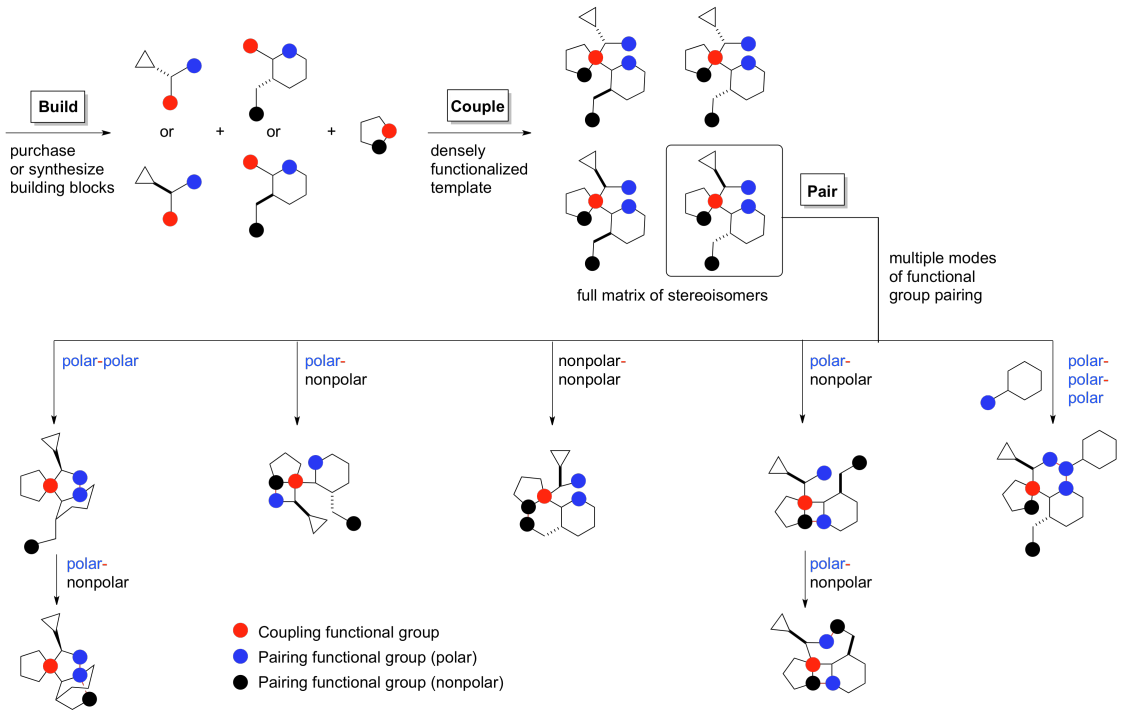
1. Application and limitations of metathesis reactions in the build/couple/pair strategy for the generation of optimal small-molecule screening collections

One of the most challenging problems that organic chemists face is the need to generate optimal small-molecule screening collections capable of probing normal and disease-associated biological processes. As described in a recent review,[1] "the development of effective small-molecule probes and drugs entails at least three stages: 1) a discovery phase, often requiring the synthesis and screening of candidate compounds, 2) an optimization phase, requiring the synthesis and analysis of structural variants, 3) and a manufacturing phase, requiring the efficient, large-scale synthesis of the optimized probe or drug". Therefore, a new type of synthetic chemistry aimed at yielding small molecules that increases the probability of success in all three phases should be developed. Although such transformative chemistry has historically proven difficult to achieve, a novel strategy in diversity-oriented synthesis (DOS)[2] called build/couple/pair (B/C/P) has emerged, which may have the potential to achieve these goals.

In the "build" phase (Scheme **I-1**), building blocks containing orthogonal sets of functional groups suitable for subsequent coupling and pairing reactions are bought or synthesized. For chiral building blocks, obtaining all possible stereoisomers in their enantiopure form is a requirement. In the "couple" phase, intermolecular coupling reactions are performed to join the building blocks together either without the creation of new stereogenic elements or with complete control of all possible stereochemical outcomes. In the "pair" phase, intramolecular functional-group-pairing reactions[3] are

performed. In this strategy, molecular complexity is generated in pairing reactions and sometimes in coupling reactions as well. Stereochemical diversity is incorporated in the build and couple phases, while skeletal diversity is achieved through the different combinations of pairing reactions between polar and polar, polar and nonpolar, or nonpolar and nonpolar functional groups. Overall, this strategy integrates complexity-generating reactions with diversity-generating processes[4] by focusing on making the product of one reaction the substrate of a diverse range of subsequent pairing reactions.[5]

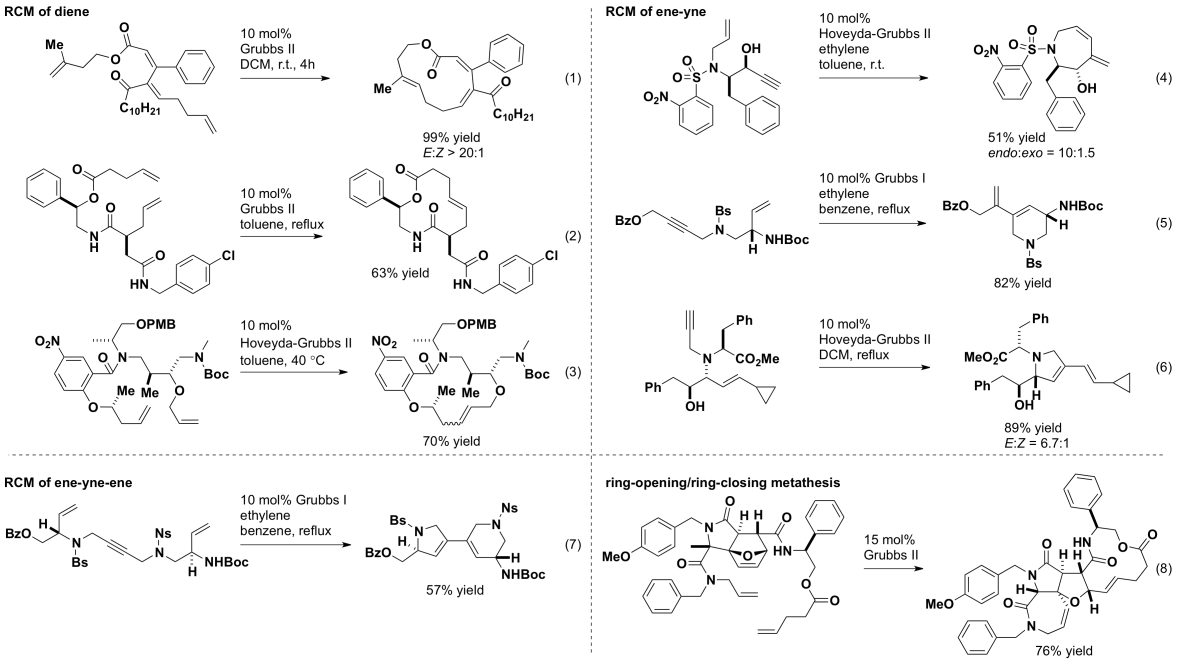
Scheme I-1. Illustration of the build/couple/pair strategy (adapted from ref. 1).



In practice, when applying the build/couple/pair strategy to generate diverse, small-molecule screening collections, it is necessary to consider the qualities of an ideal functional group pairing reaction. There are two criteria by which such a reaction can be

evaluated. First, the reaction used for pairing should be highly general over a wide range of substrates. By carefully studying previous works, we recognized that ring-closing metathesis (RCM) was widely used as a pairing reaction due to its generality and robustness. Besides forming cyclic structures with various ring sizes, metathesis reactions can provide skeletal diversity starting from different substrates (Scheme **I-2**). RCM produces a cyclic alkene from a diene (eq. 1,[6] eq. 2,[7] eq. 3[8]), a cyclic diene from an ene-yne (eq. 4,[9] eq. 5,[10] eq. 6[11]) and a bicyclic diene from an ene-yne-ene (eq. 7[10]). Moreover, a ring-opening/ring-closing cascade can generate polycyclic structures (eq. 8[12]).

Scheme I-2. Skeletal diversity generated from different types of RCM reactions.



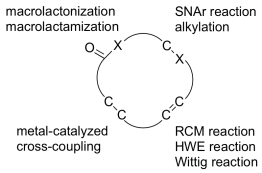
In addition to substrate generality and diversity, reactions yielding products that are in turn poised for further transformations are also desired. The ideal situation arises when the functional group(s) created by a highly general reaction is itself a substrate for an

array of synthetic transformations. For example, a β-hydroxy carbonyl moiety generated from an aldol reaction can be dehydrated, alkylated, reduced, or oxidized to provide different functionalities and the potential for further transformations. The diversification potential of such intermediates allows the efficient generation of analogues that are useful for the study of structure-activity relationships. Moreover, this potential also facilitates the medicinal chemistry effort to tune the physicochemical properties of a hit compound. Following this criterion, we became conscious of the fact that RCM products offer relatively few opportunities for further modification. We therefore initiated several research projects with the goal of expanding the diversification potential of the RCM products to further increase the utility of this reaction.

2. RCM of dienes to build naturally occurring and novel macrocyclic compounds

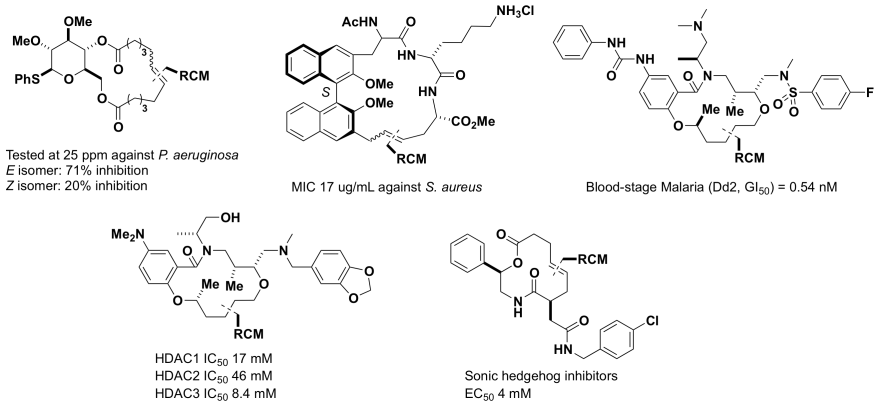
We initially focused on macrocyclic RCM of diolefinic substrates. Macrocyclic compounds (with ring sizes larger than or equal to 8) are important naturally occurring small molecules produced by various organisms during the course of evolution. These macrocycles usually display interesting biological activities.[13-33] A number of them and their analogues have been in use as therapeutics for years and include antibiotics (erythromycin,[34] rifamycins,[35,36] colistin[37,38], daptomycin[39], and vancomycin[40-42]), antifungals (amphotericin B[43]), immunosuppressants (sirolimus,[44,45] and cyclosporine[46,47]), and cancer therapies (azaepothilone B[48] and sirolimus[49-51]). Due to the biological activity and structural complexity of macrocyclic compounds, they represent an attractive and challenging class of compounds for organic chemists to synthesize.

Figure I-1. Summary of typical macrocyclization reactions.



There are indirect ways to form macrocycles,[52] yet the most efficient method is macrocyclization. In theory, any reaction that couples two parts of a linear molecule together can be used as a macrocyclization reaction. However in practice, only a small number of reactions have been developed and extensively used by organic chemists in this respect. Typical macrocyclization reactions (Figure **I-1**) include lactonization,[53-57] lactamization,[56,58-63] alkylation,[64-70] S_NAr reactions,[71-74] Horner-Wadsworth-Emmons or Wittig reactions,[75-77] transition metal-catalyzed coupling reaction,[78-90] and alkene ring-closing metathesis.[91-116] Other types of reactions such as ring-closing alkyne metathesis (RCAM),[92,94,95,117] cycloaddition,[118-122] oxidative lactonization,[123,124] Prins-type reactions,[125] and multicomponent cyclizations[126-128] have also been recently explored. Among these transformations, RCM of diolefinic compounds is an attractive methodology for three major reasons. First, olefins are orthogonal to a number of common reactions and so rarely require protection. Second, reaction conditions of RCM are relatively mild, thus common functional groups (as well as protecting groups) are compatible under these conditions. Third, RCM is a catalyzed reaction that does not typically need any activating reagents. Therefore, since the commercialization of metathesis catalysts,[129-131] the applications of RCM in synthesizing macrocyclic compounds have been extensively explored.

Figure I-2. Representative bioactive synthetic macrocycles made from RCM reactions.



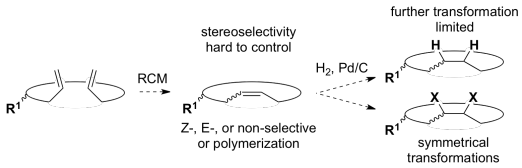
In addition to the total synthesis of macrocyclic natural products and their analogues, there has been interest in accessing non-naturally occurring macrocycles using RCM reactions in search for novel biological activities.[98,99,101,107,109,111,114,132-136] Screening of such compounds has successfully yielded compounds that have novel antibiotic activities[137-139] as well as activities against different types of biological targets including histone deacetylases[8,140,141] and sonic hedgehog[7] (Figure **I-2**). Moreover, macrocyclic RCM reactions have been extensively used in medicinal chemistry to cyclize precursors in order to improve target affinity and selectivity, as well as bioavailability and stability.[142-150] Within our own laboratories, macrocyclic RCM has proven to be an enabling methodology toward the goal of assembling small-molecule screening collections to probe normal and disease-associated biological processes.[7,8,12,151-153]

3. Limitations of ring-closing metathesis towards the generation of macrocyclic compounds and previous approaches to address them

In efforts to synthesize macrocyclic compounds via RCM reactions, we have recognized two major limitations: lack of control over the stereochemistry of olefin product and limited potential for further transformations on the olefin moiety (Scheme **I-3**).

First, controlling the stereochemistry of the resulting olefin is often problematic.[103,105,106] Under the circumstances when the olefin moiety is not required for further transformation or in the final compound, the stereoselectivity generally will not be an issue after reduction of the double bond. On the contrary when the olefin moiety is crucial, it is often challenging to separate the desired stereoisomer from the mixture at the cost of the undesired isomer.[154-161] In some extreme cases when the RCM reactions only generated the undesired stereoisomers, extra synthetic steps to produce the desired alkene configuration are required[162] or the synthetic route has to be redesigned.[77,163] Since a variety of factors can determine the stereochemical outcome in RCM reactions,[76,103,106] general strategies that give rise to either *Z* or *E* olefins remain a significant challenge.

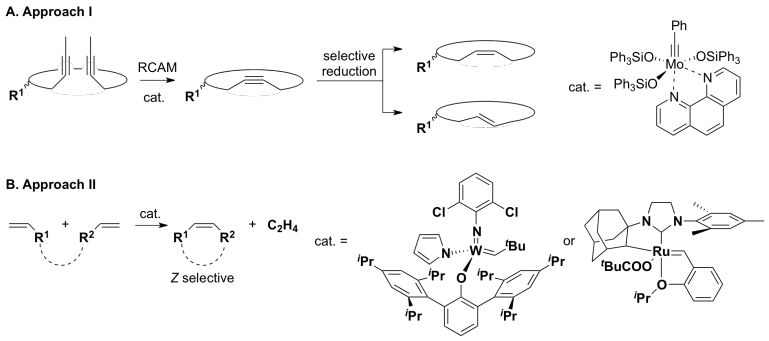
Scheme I-3. Limitations in macrocyclic RCM of diolefinic compounds.



Two major advances that address the stereoselectivity of macrocyclic RCM reactions have been achieved. One approach involves ring-closing alkyne metathesis and selective reduction of the macrocyclic alkyne intermediate to yield *Z* or *E* olefins (Scheme **I-4**, **A**).[164-167] However, this approach is only applicable to ring sizes of 12 and larger due to

the ring strains of cyclic alkynes.[168,169] Another approach is based on the development of *Z*-selective catalysts that have been successfully applied in cross-metathesis (CM) reactions and macrocyclic RCM reactions (Scheme **I-4**, **B**);[170-174] however, catalysts that yield the *E* olefin product selectively have yet to be discovered.

Scheme I-4. Two approaches to solve the stereoselectivity issue of macrocyclic RCM reactions.



The second limitation of macrocyclic RCM is that, as mentioned above, there are few opportunities for further modification. The sp^2 carbon atoms in a cyclic 1,2-disubstituted olefin (the typical RCM product) are not easily chemically differentiated. In the absence of a dominant steric or electronic bias within the substrate, achieving regioselectivity on such a product is problematic (e.g. in a hydroboration reaction). Due to this drawback, post-metathesis functionalizations have predominantly been confined to "symmetrical" transformations (Scheme **I-3**) such as hydrogenation, dihydroxylation,[175-177] epoxidation,[154,177,178] and aziridination.[179,180]

4. Our proposed approach to address both the stereoselectivity and the post-RCM functionalization simultaneously by using a versatile silyl group (the major focus of this chapter)

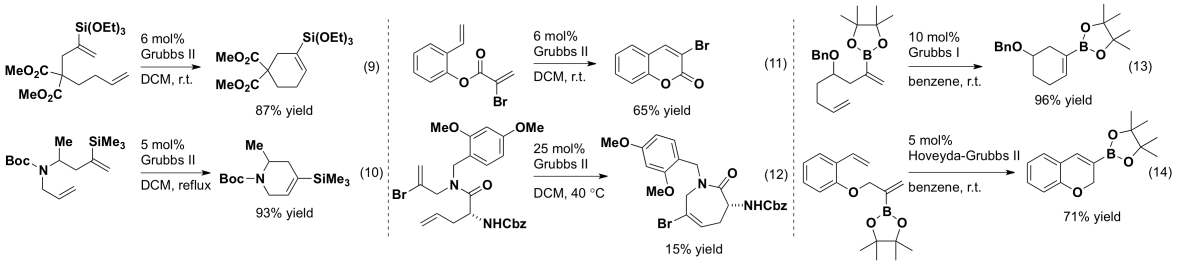
To address both limitations, we investigated the introduction of a chemical handle at the internal position of one of the olefins. Such geminal-disubstituted olefins could generate cyclic trisubstituted alkenes upon the treatment with a RCM catalyst. First, the sterics of the exocyclic chemical handle would be expected to favor formation of the *E* product (assuming it is larger than a methylene group). Second, it would allow subsequent functionalization of the product that is not limited to "symmetrical" transformations.

Aryl groups,[181-184] carbonyl groups,[185-193] silicon groups,[194-199] boron groups,[200,201] alkoxy groups,[202-207] halogens,[208-213] nitrogen,[214,215] and phosphinate[216] can be incorporated into the internal position of one of the olefins yielding a variety of trisubstituted alkene products. Yet to our knowledge, most of these precedents were limited to making small rings (5-, 6-, or 7-membered) and not macrocycles. It has been shown that alkyl groups (a methyl or ethyl group) can be installed to access trisubstituted macrocycles. However, they failed to control the stereoselectivity of the reaction[154,161,217]

Among these explorations, we are especially interested in the cases when a non-carbon substituent was employed (Scheme **I-5**). Advantages of having exocyclic silicon (eq. 9,[197,198] eq. 10[196]), bromide (eq. 11,[213] eq. 12[212]), or boron (eq. 13,[200] eq. 14[201]) attached to the alkenes in the product are due to the versatile nature of such groups. *Ipso*-protonation reactions (protodesilylation, protodebromination, protodeboronation) generate simple

disubstituted alkenes. Oxidation of alkenylsiloxanes and alkenylboronates yields ketones; of alkenyl bromide yields α-bromoketones. Most importantly, all of these functional groups can participate in transition-metal catalyzed coupling reactions, which enables diversification of the substituted alkenes in a regiospecific manner.

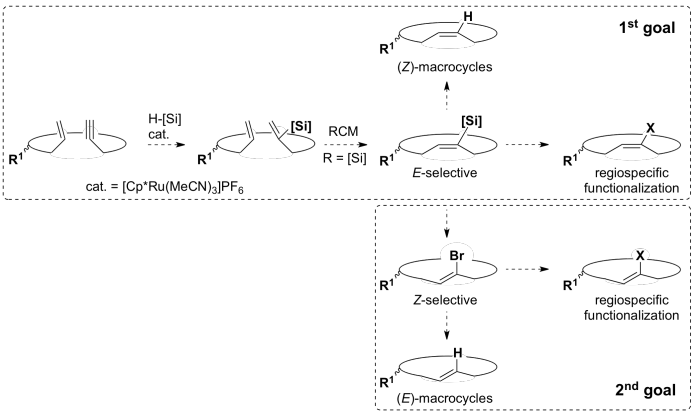
Scheme I-5. RCM of vinyl halides, vinylboronates, and vinylsilanes to make trisubstituted cyclic alkenes.



Our detailed proposal is described in Scheme **I-6**. Silyl groups were selected in our study owing to several reasons. First, the inclusion of a silyl group at the internal carbon of one of the olefins could be easily achieved via a regioselective hydrosilylation reaction of a terminal alkyne. A ruthenium-based catalyst developed in the Trost group is able to achieve this transformation with high chemo- and regio-selectivity, good functional group compatibility, and broad silyl group generality.[197,198] Second, silylalkene groups are, in general, compatible with metathesis catalysts compared to bromoalkenes.[218] Third, silyl groups are easier to handle and more stable than boryl groups. We also hypothesized that the steric bulk of the silyl group would likely control the stereoselectivity of the RCM reaction yielding the *E* product (Scheme **I-6**, the 1st goal). Moreover, if the (*E*)-alkenylsiloxane can be transformed to the *Z*-trisubstituted alkenyl bromide (the 2nd goal),

we would not only obtain both stereoisomers, but also introduce great potential for further diversification of both stereoisomers.

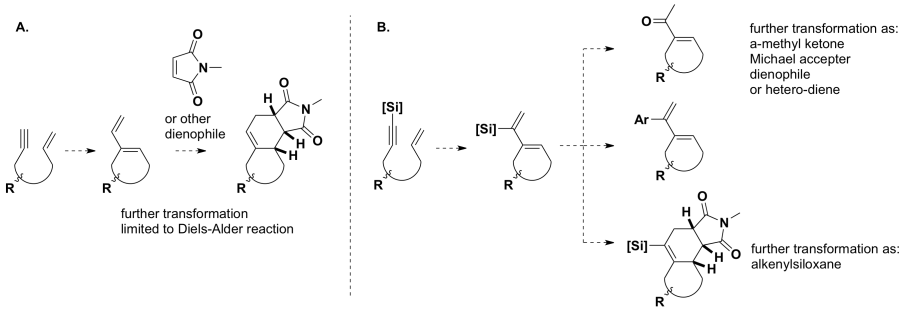
Scheme I-6. Expanding the scope of RCM reations through silyl group incorporation.



5. Applications of silyl groups in other types of RCM reactions

Given the versatility of the silyl group, another research project was also launched in our group to explore its potential in ene-yne RCM reactions.

Scheme I-7. Extension of the ene-yne RCM reaction by the introduction of a silyl group.

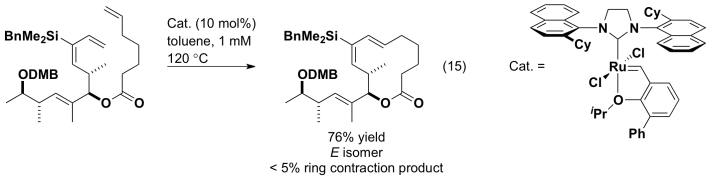


Ene-yne RCM reactions are powerful transformations to generate cyclic dienes. Without a functional group on the resulting diene, the most common way of further transforming

it was a Diels-Alder reaction (Scheme **I-7**, **A**). The incorporation of a silyl group on the alkyne moiety for ene-yne RCM was already reported but not well studied.[219-226] The silyl group that ends up on the diene can be oxidized to generate an enone moiety (Scheme **I-7**, **B**), which serves as a dienophile or hetero-diene as well as a Michael accepter. In addition, metal-catalyzed cross-coupling reactions can convert the silyl group to a variety of aromatic groups. The Diels-Alder reaction is still applicable but with the benefit of leaving a valuable alkenylsiloxane moiety for further transformations.

Concurrent with our studies of macrocyclic RCM of vinylsiloxanes, the Fürstner group demonstrated the use of silyl groups in macrocyclic diene-ene RCM.[227] By installing the silyl group on the C3 position of a terminal butadiene (Scheme **I-8**, eq. 15), they were able to control the stereochemical outcome of the macrocyclic RCM reaction (in this case *E*-selective) and prevent ring contraction to form the 10-membered ring (the reaction with the internal alkene of the diene) observed in the absence of the silyl group.

Scheme I-8. An example of the use of silyl groups in macrocyclic diene-ene RCM.



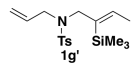
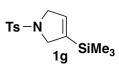
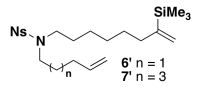
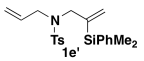
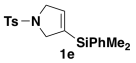
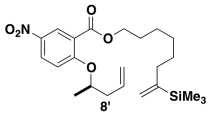
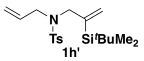
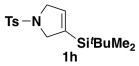
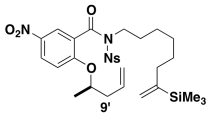
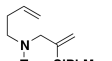
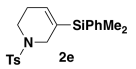
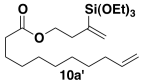
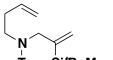
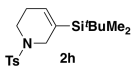
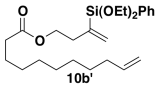
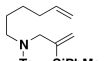
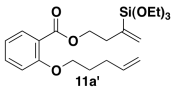
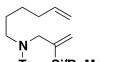
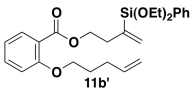
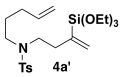
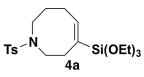
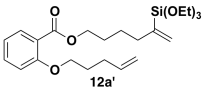
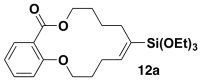
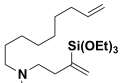
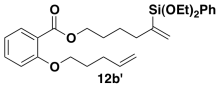
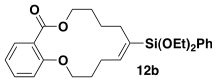
Chapter I-2. Ring-Closing Metathesis of Vinylsilanes and Vinylsiloxanes

1. Initial attempt of RCM of vinylsilanes and vinylsiloxanes to form small rings and macrocycles

As shown in Table **I-1**, Dr. Masaaki Hirano pioneered the RCM of trimethylvinylsilane **1g'** to form a 5-membered ring. Mr. Miguel Jimenez and I explored the RCM of dimethylphenylsilanes **1e'** or **2e'** and *tert*-butyldimethylsilanes **1h'** or **2h'** to form 5- or 6-membered rings. In accordance with previous reports, all substrates were successfully closed although the yields of different substrates varied. However, 8-membered rings bearing either silyl group, substrate **3e'** and **3h'** failed to undergo ring-closing metathesis.

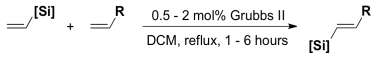
At the same time, Mr. Anders S. Hansen and Dr. Eun-Ang Raiber were attempting the RCM of vinylsilanes **6'** or **7'** to form 12- or 14-membered rings. Various reaction conditions were applied, but none of them were effective. Next they tried to introduce a rigidifying element to favour the ring closure. Substrates **8'** and **9'** were synthesized and subjected to various reaction conditions. However, no desired 15-membered products were observed under any condition. In most of the unsuccessful cases, incomplete conversion and decomposition of starting materials were observed.

Table I-1. Initial exploration on RCM of vinylsilanes and vinylsiloxanes to make small rings and macrocycles with various silyl groups and reaction conditions.

Substrate	Product	Y.[b] (%)	Rxn cond.[a]	Substrate	Product	Y.[b] (%)	Rxn cond.[a]
 1g'	 1g	95	**A**	 6' n = 1 7' n = 3	not observed	-	**C**, **D**, **E**, **F**, **G**, **H**, **I**
 1e'	 1e	92	**A**	 8'	not observed	-	**H**, **I**, **J**
 1h'	 1h	81	**B**	 9'	not observed	-	**H**, **I**, **K**
 2e'	 2e	95	**A**	 10a'	not observed	-	**B**, **L**
 2h'	 2h	44	**B**	 10b'	not observed	-	**B**, **L**
 3e'	not observed	-	**B**	 11a'	not observed	-	**B**
 3h'	not observed	-	**B**	 11b'	not observed	-	**B**
 4a'	 4a	20[c]	**B**	 12a'	 12a	27[c]	**C**
 5'	not observed	-	**B**	 12b'	 12b	2[c]	**C**

[a] Reaction conditions: **A**. Grubbs II 10 mol%, DCM (20 mM), r.t., 18 h; **B**. Grubbs II 20 mol%, DCM (3 mM), reflux, 18 h; **C**. Grubbs II 10 mol%, DCM (2 mM), reflux, 10 h; **D**. Hoveyda-Grubbs II 20 mol%, DCM (1.7 mM), reflux, 24 h; **E**. Grubbs II 10 mol%, toluene (2 mM), 65 °C, 18 h; **F**. Grubbs I 10 mol%, DCM (1.8 mM), reflux, 18 h; **G**. Grubbs II 20 mol%, toluene (3 mM), 300 W Microwave, 100 °C, 30 min/cycle, 3 cycles; **H**. Schrock's Mo-based catalyst 50 mol%, DCM (2.6 mM), r.t., 18 h; **I**. Schrock's Mo-based catalyst 50 mol%, toluene (2.6 mM), 45 °C, 18 h; **J**. Hoveyda-Grubbs II 20 mol%, toluene (1.7 mM), 60 °C, 24 h; **K**. Hoveyda-Grubbs II 20 mol%, toluene (1 mM), 300 W Microwave, 100 °C, 30 min/cycle, 3 cycles; **L**. the isolated homodimers were resubmitted to condition C with 6 mol% Grubbs II catalyst added in 2 times. [b] Isolated yield unless otherwise indicated. [c] Yield determined by ^{1}H NMR analysis.

Table I-2. Influence of the silyl group in CM reactions.



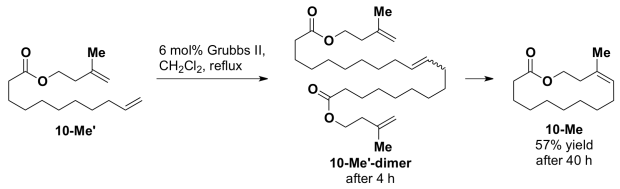
Entry	-[Si]	-R	Yield (%)
1	$Si(OEt)_3$	Ph	80
2	$SiCl_3$	Ph	83
3	$Si(OAc)_3$	Ph	75
4	$Si(OEt)_2Me$	Ph	6
5	$Si(OEt)Me_2$	Ph	5
6	$SiMe_3$	Ph	0
7	$SiPh_3$	C_4H_9	0
8	$Si(C_6H_4\text{-}Me\text{-}p)_3$	C_4H_9	0
9	$Si(C_6H_4\text{-}CF_3\text{-}p)_3$	C_4H_9	97

This result drew our attention the role of the silyl group. Although the influence of different silyl groups had not been extensively studied for RCM, there were ample precedents in the area of cross metathesis (CM). Pietraszuk *et al.* demonstrated that the influence of the silyl groups on CM largely originates from an electronic effect of the substituents on silicon (Table **I-2**).[228-235] Silyl groups with electronegative substituents such as EtO-, AcO-, Cl- gave better yields than with Me- and/or Ph- groups (entry **1**-**3** versus **6**, **7**). The use of $(p\text{-}CF_3Ph)_3Si$- led to quantitative yield in the CM reaction with 1-hexene (entry **9**) while the use of Ph_3Si- or $(p\text{-}MePh)_3Si$- did not produce any detectable product (entry **7** and **8**). With this knowledge, we decided to pursue a substrate, that had been shown to undergo RCM to give a trisubstituted macrocycle (Scheme **I-9**),[217] with alkoxysilyl groups (**10a'** and **10b'**) instead of the original methyl group (**10-Me'**).

The initial attempts to close substrate **10a'** and **10b'** were not successful under condition **B** and only homodimers were isolated. Through personal contact with Prof. Fürstner by Dr. Raiber, it was found out that in order to close substrate **10-Me'**, homodimers needed to be separated and resubmitted to the RCM reaction using Grubbs II as catalyst.

However following this procedure (Table **I-1**, condition **L**), they were still unable to cyclize either substrate.

Scheme I-9. Reported RCM to form macrocyclic trisubstituted alkenes (adapted from ref 181).



Despite those unsuccessful attempts, Mr. Miguel Jimenez and I were able to obtain an 8-membered ring **4a** with a triethoxysilyl group. In contrast, substrate **5'** failed to yield the 12-membered product. Dr. Eun-Ang Raiber and I decided to revisit the salicylate-based substrates. Compounds **11a'** and **11b'** were made separately and submitted to RCM reactions. However, both failed to give any cyclized products. We then increased the ring size from 12 to 14 by inserting an ethylene group into the substrates. Finally, substrate **12a'** with a triethoxysilyl group was successfully closed to generate the 14-membered macrocyclic alkenylsiloxane **12a** under un-optimized reaction conditions with 27% ^{1}H NMR yield. Surprisingly, the analogue **12b'** with a diethoxyphenylsilyl group yielded only 2% of the desired product **12b** under the same reaction conditions.

This initial exploration taught us several lessons. First, macrocyclic RCM of vinylsiloxanes is possible. However, typical RCM conditions are not optimal. Second, ring sizes of the products seem to affect the outcome of the reaction, and so far only 8-

and 14-membered macrocycles were formed. Finally, the silyl groups played an important role in this reaction, which might be more complicated than a purely electronic effect in CM reactions. With this knowledge in mind, I decided to move forward to systematic optimization of the reaction conditions.

2. Screening catalysts and optimizing reaction conditions for RCM of vinylsiloxanes to make macrocycles

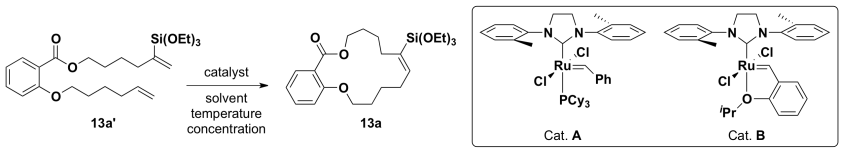
Substrate **13a'** (an analogue of **12a'** with an extra methylene group) was synthesized and subjected to the initial conditions. Not surprisingly, the yield of the 15-membered product **13a** dropped to 3% (Table **I-3**, Entry **2**). This demanding substrate was then used to optimize the reaction conditions.

Among commercially available ruthenium-based metathesis catalysts, catalyst **A** was able to increase the yield from 3% to 19% under the original reaction conditions. In contrast to the second-generation Grubbs catalyst, **A** bears one methyl group on the *ortho*-position of each phenyl ring, making it less sterically hindered and more reactive.[236] After varying solvent, temperature, and concentration we found that optimal results (63%, ^{1}H NMR yield) were obtained using benzene or toluene as solvent at 35 °C and with 20 mol% of catalyst **A** (Table **I-3**, Entry **11** and **12**).

Under the optimal reaction conditions, unreacted starting material was still observed, indicating that the catalyst was deactivated before the reaction went to completion. It is very likely that C(sp^2)-H bond insertion of the *N*-aryl ring on the ligand by ruthenium can

lead to fast deactivation of catalyst **A**,[237] in addition to the commonly observed decomposition pathways of Grubbs II.[238]

Table I-3. Catalysts screening and reaction condition optimization.



Entry	Catalyst	Solv.	Temp. (^{o}C)	Conc. (mM)	Yield (%)[a]
1	Grubbs I	DCM	reflux	2	< 2
2	Grubbs II	DCM	reflux	2	3
3	Hoveyda-Grubbs I	DCM	reflux	2	< 2
4	Hoveyda-Grubbs II	DCM	reflux	2	< 2
5	**A**	DCM	reflux	2	19
6	**B**	DCM	reflux	2	3
7	**A**	$ClCH_2CH_2Cl$	50	2	15
8	**A**	benzene	50	2	54
9	**A**	toluene	50	2	50
10	**A**	benzene	23	2	42
11	**A**	benzene	30	2	63
12	**A**	benzene	40	2	63
13	**A**	benzene	60	2	45
14	**A**	benzene	35	1	52
15	**A**	benzene	35	5	39
16	**A**	benzene	35	10	20
17	**A**	benzene	35	20	12

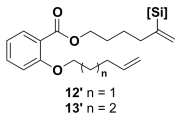
[a] Yield determined by ^{1}H NMR analysis.

3. Influence of silyl groups on the reaction outcome

We next examined the influence of different silyl groups on the yield of the RCM reaction (Table **I-4**). The results are in alignment with those of CM reactions. Generally, ethoxy substituents promote the formation of product and lead to higher yields compared to alkyl and/or aryl substituents (compare **a-d** with **e**, **f**). More ethoxy substituents are preferred over less (compare **c** with **d**). Pietraszuk *et al.* noted that electron-withdrawing substituents shut down an undesired pathway that leads to catalyst deactivation.[228,230] We suggest that these unproductive processes are operative in macrocyclization reactions as

well and require the appropriate siloxane group to suppress them. However, in contrast to the CM precedents, the sterics of the silyl group also influenced the yield of the reaction. This effect is seen with the more demanding substrates **13a'**-**13f'**, while substrates **12a'**-**12f'** show the same trend but to a lesser degree. When one of the ethoxy substituents was changed to a methyl group (**13a'** versus **13c'**), the yield was improved while a change to a phenyl group (**13c'** versus **13b'**) resulted in the yield being halved. Our results indicate that the diethoxymethylsilyl group delivers the best reaction outcomes by maintaining a balance between both steric and electronic effects.

Table I-4. Influence of the silicon substituents on the yield of RCM.

Substrate	Entry	Silyl group	**12**[a]	**13**[a]
 **12'** n = 1 **13'** n = 2	a	$Si(OEt)_3$	92	60
	b	$Si(OEt)_2Ph$	69[b]	35[b]
	c	$Si(OEt)_2Me$	95	76
	d	$Si(OEt)Me_2$	81	62[b]
	e	$SiMe_2Ph$	54 (71[b])	32
	f	$SiEt_3$	10[b]	< 2

[a] Isolated yield (%) unless otherwise indicated; [b] yield calculated based on ^{1}H NMR analysis of reaction mixtures.

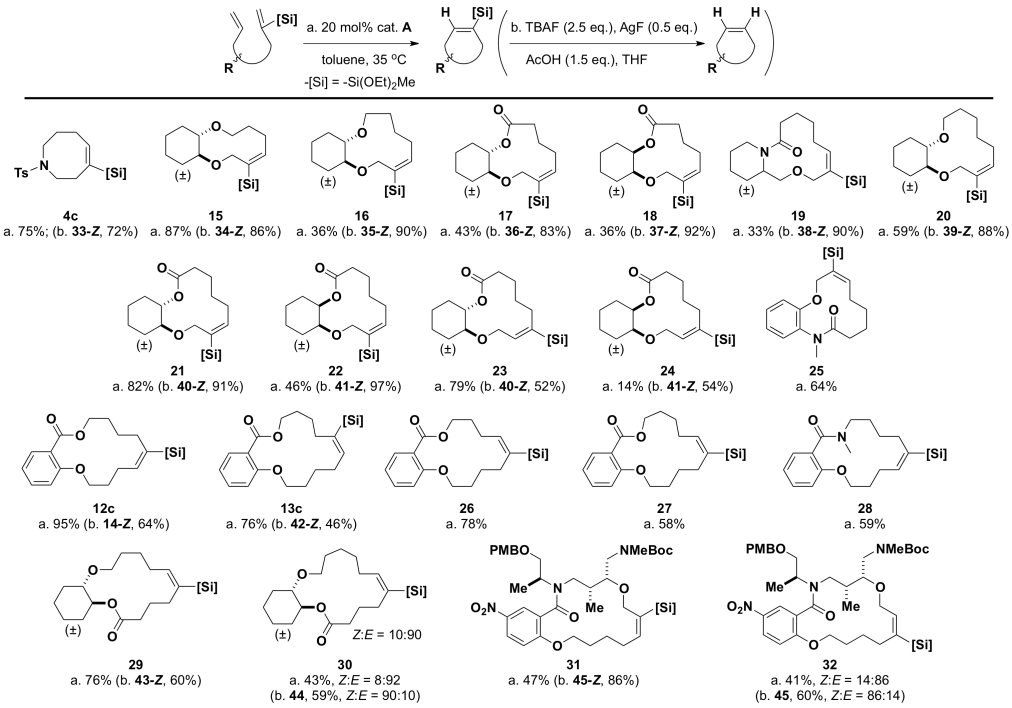
Vinylsiloxanes and alkenylsiloxanes are stable toward column chromatography and can be stored at -20 °C for 6 months without significant decomposition.

4. Substrate generality study and protodesilylation

Using the diethoxymethylsilyl group, macrocyclic alkenyl siloxane products with a wide range of ring sizes were obtained in moderate to excellent yields (Scheme **I-10**). Diastereomers gave differing yields of purified products. For some substrates, silyl groups were incorporated into each of the alkene termini of the diene substrates. The *trans*-cyclohexanediols with silyl groups on different termini behaved similarly (**21** and

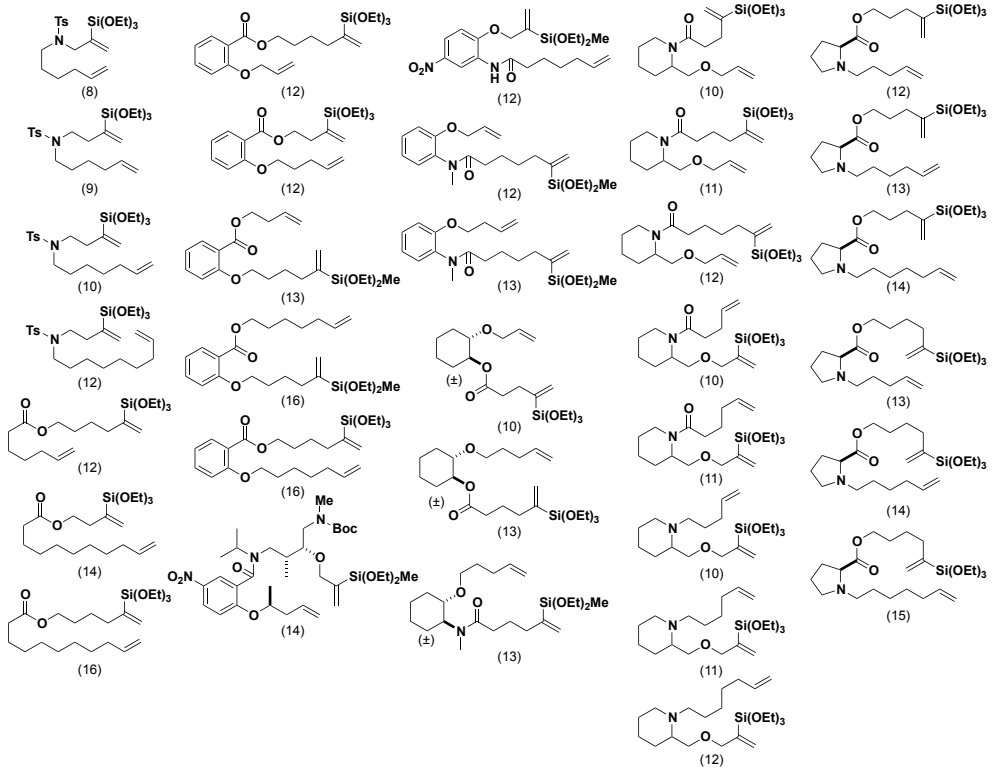
23); while the silyl regioisomers of *cis*-cyclohexanediols behaved differently (**22** and **24**). To test the generality of this method in more complex molecules, two substrates inspired by previous work[8] were prepared, incorporating vinylsiloxanes on either alkene termini. The 16-membered rings were both formed in moderate yields (**32** and **33**).

Scheme I-10. Isolated yields of the RCM of various substrates and protodesilylation of the alkenyl siloxane products (in parentheses).



All corresponding *Z*-disubstituted olefins were obtained by protodesilylation with good to excellent yields while maintaining the geometry of the olefins. As envisaged, the tri-substituted olefins in the macrocyclic products have the *E* configuration (except for **30** and **32** that are mixtures of both stereoisomers with high *E* selectivity).

Scheme I-11. Substrates that failed to be cyclized under sub-optimal reaction conditions with ring sizes of desired products (in parentheses).



Substrates with silyl groups that failed to be closed are listed in Scheme **I-11**. Although these substrates were not subjected to the optimum reaction conditions (50 °C for some substrates, and $Si(OEt)_3$ instead of $Si(OEt)_2Me$), the introduction of the silyl group did not result in productive RCM. We do not know whether the non-silylated analogues of these substrates are competent to undergo RCM to generate the desired macrocycles if the ring strains associated with the formation of the macrocycles are intrinsically high (see discussion in Chapter **I-2-7**). Regarding instances when the silyl group thwarts ring closure, it may result from transannular interactions introduced by the silyl group which disfavor the formation of the macrocycle. A more comprehensive mechanistic

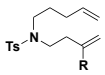
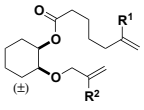
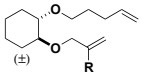
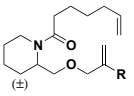
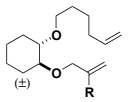
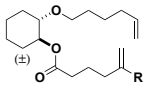
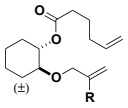
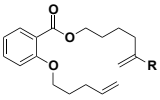
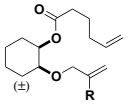
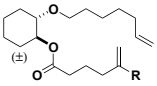
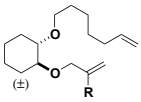
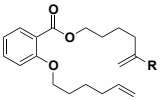
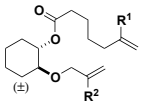
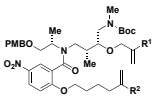
investigation into the factors governing the outcomes of these reactions is warranted. In order to close these recalcitrant substrates, higher reaction temperature might be required. However, the catalyst decomposes faster at higher temperatures. Therefore, future work or collaboration should involve the development of more stable catalyst that can improve the generality of this methodology.

5. Role of silyl groups in controlling stereochemistry of the reaction

We next sought to understand the role of the silyl group in controlling the stereochemical outcome of the reaction. For comparison, most of the corresponding simple (non-silyl containing) RCM precursors were synthesized in order to determine the intrinsic stereoselectivity of the substrates (Table **I-5**). Upon treatment with the optimized reaction conditions as well as typical RCM conditions using Grubbs II, *Z*-selective, *E*-selective, and non-selective outcomes were all observed. For the *Z*-selective (**33'**, **34'**, **38'**, **39'**, **40'**, **43'**, and **14'**) or non-selective (**42'**) simple olefin substrates, the introduction of the silyl group was found to reinforce the intrinsic stereoselectivity. More dramatically, for the *E*-selective substrates (**36'**, **37'**, **41'**, **44'**, and **45'**), the introduction of silyl groups in the substrates (**17'**, **18'**, **22'**, **24'**, **30'**, **31'**, and **32'**) can completely override the intrinsic preferences and generate the *E*-trisubstituted products (with *Z* configuration after protodesilylation). This confirmed our initial hypothesis that a silyl group serves as an effective controlling group favoring the formation of the *E* product in macrocyclic RCM reactions. During this comparative study, it was noticed that the RCM of simple olefin substrate gave rise to complex mixture of products in some cases. This observation

promoted us to explore and understand another important role of the silyl group. For a detailed explanation, see Chapter **I-2-7**.

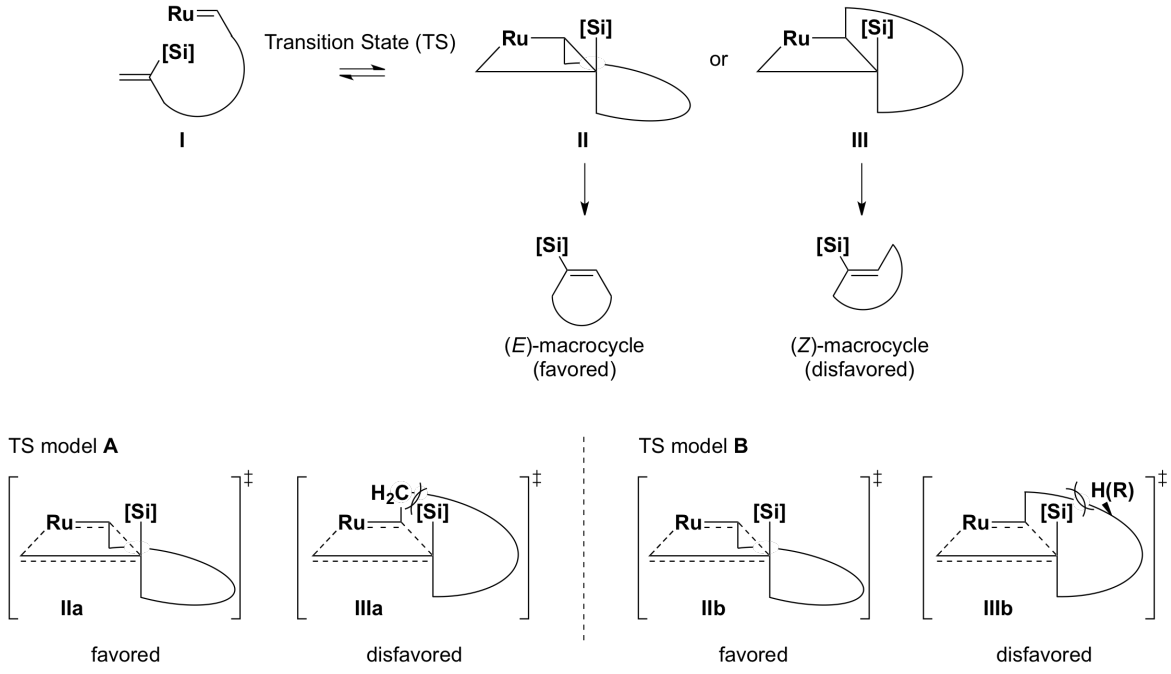
Table I-5. Influence of the silyl group on the specificity and stereoselectivity of RCM reactions.

Substrate	#	R	Cond. **I**[a]	Cond. **II**[a]	Substrate	#	R	Cond. **I**[a]	Cond. **II**[a]
							R^1 R^2		
	**4c'**	[Si][b]	*Z*[c]	-		**24'**	Si H	*Z*	-
	33'	H	*Z*	*Z*		**22'**	H Si	*Z*	-
						41'	H H	c. mix. (19:81)	c. mix. (19:81)
	**15'**	[Si]	*Z*	-		**19'**	[Si]	*Z*	-
	34'	H	c. mix.[d] (*Z*)[e]	c. mix. (*Z*)		**38'**	H	c. mix. (*Z*)	c. mix. (*Z*)
	**16'**	[Si]	*Z*	-		**29'**	[Si]	*Z*	-
	35'	H	c. mix.	c. mix.		**43'**	H	c. mix. (76:24)	c. mix. (76:24)
	**17'**	[Si]	*Z*	-		**12c'**	[Si]	*Z*	-
	36'	H	c. mix. (24:76)	c. mix. (24:76)		**14'**	H	81:19[f]	80:20[g]
	**18'**	[Si]	*Z*	-		**30'**	[Si]	90:10	-
	37'	H	*E*	*E*		**44'**	H	28:72	24:76
	**20'**	[Si]	*Z*	-		**13c'**	[Si]	*Z*	-
	39'	H	c. mix. (*Z*)	c. mix. (*Z*)		**42'**	H	57:43[f]	54:46[g]
		R^1 R^2					R^1 R^2		
	**23'**	Si H	*Z*	-		**31'**	Si H	*Z*	-
	21'	H Si	*Z*	-		**32'**	H Si	86:14	-
	40'	H H	c. mix. (*Z*)	c. mix. (*Z*)		**45'**	H H	36:64	-

[a] Cond. **I**: cat. **A** (20 mol%), toluene, 35 °C; Cond. **II**: Grubbs II (10 mol%), 1,4-benzoquinone (20 mol%), toluene, 35 °C; [b] [Si] equals diethoxymethylsilyl. For silylated substrates, *Z*:*E* assignment is based on the protodesilylated products; [c] Single stereoisomer reported for *Z*:*E* ratios >98:2, otherwise *Z*:*E* ratio was determined by ^{1}H NMR analysis of the crude mixture; [d] c. mix.: complex mixture of products (cyclized and uncyclized oligomers); [e] stereochemistry of cyclized monomer reported in parentheses whenever its proportion within the complex mixture was sufficient for determination; [f] reactions performed at room temperature; [g] reactions performed in refluxing DCM.

6. Proposed models to explain the stereoselectivity controlled by the silyl group

Scheme I-12. Two proposed models to explain the stereoselectivity of the RCM reaction.



Based on previous studies on CM by Grubbs and coworkers[239] as well as our own observations, the initiation of the reaction would most likely happen on the simple olefin (for detailed discussion, see Chapter **I-2-7**). After the formation of **I**, we propose metallocyclobutane intermediates **II** is preferably formed leading to the *E* product (Scheme **I-12**). There are two models that can explain the high selectivity observed. As shown in model **A**, the allylic carbon in transition state (TS) **IIa** avoids steric interactions with the bulky silyl group as in TS **IIIa**. Thus the formation of intermediate **II** is favored. To support this model, CM of a geminal-disubstituted vinylsiloxane and a simple mono-substituted olefin was performed (see Chapter **I-5-2**). Without the influence imposed by the macrocycle, the stereoselectivity of the CM reaction will only reflect the interaction between the silyl group and the allylic carbon. Unfortunately, the CM reactions that we

performed so far were not successful. Therefore, we looked for evidence that is consistent or in conflict with what can be inferred from model **A**. No matter which olefin terminus the silyl group is installed on, the stereoselectivity should be the same according to model **A**. However, for the complex substrate, putting the silyl group on one side, **31'**, yielded only the *E* isomer, yet putting the silyl group on the other side, **32'**, yielded mixture of both stereoisomers with *E*:*Z* ratio of 86:14 (see Table **I-5**). Based on this result, we concluded that the first model might be operative to some degree but not exclusive.

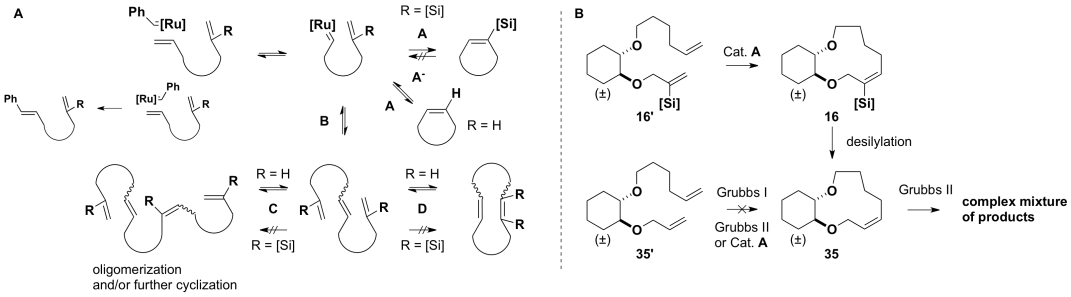
We then proposed model **B** that can explain the stereoselectivity of the reaction from a different perspective. Macrocycles are known to have transannular interactions especially when an alkene is present.[240] Depending on the macrocyclic conformation of each substrate, the energy of transition states leading to both intermediates is differentiated by transannular interactions between the silyl group and the backbone or substituent of the macrocycle. The transition state **IIIb** leading to **III** is more likely to have transannular interactions than the transition state **IIb** leading to **II** because in transition state **IIIb**, the backbone has to connect the two allylic carbons which will be on opposite faces of the metallocyclobutane ring. If this model is operating, larger rings will be able to accommodate the transition state leading to the (*Z*)-macrocycle without having severe transannular interactions. This prediction is in accordance with the results. Substrates **30'** and **32'** that form 15- or 16-membered rings gave rise to little amount of the (*Z*)-macrocycle, although the dominant products are still the *E* isomer. This model also explains that silyl groups on different olefin termini resulted in different stereoselectivities. However, model **B** is dependent on the macrocyclic conformation that

varies with different substrates. The prediction of stereoselectivity for a novel substrate will therefore not be straightforward.

7. Role of silyl groups in trapping the desired product

It is also noteworthy that several of the simple substrates gave rise to a complex mixture of products (Table **I-5**, substrates **34'**, **36'**, **38'**, **39'**, **40'**, **41'**, and **43'**), sometimes without a detectable level of cyclized monomer (substrate **35'**). The LC-MS analysis of the crude reaction indicated the formation of cyclized dimers and other polymeric by-products. This is a general problem for macrocyclic RCM reactions of simple olefins.[241-243] While the reaction conditions for the simple substrates were not optimized, these results point to the additional ability of the silyl group to suppress the formation of undesired products.

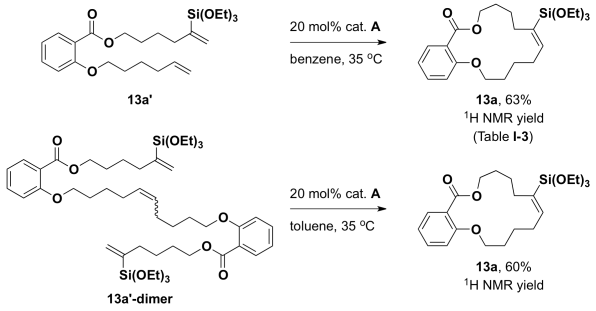
Scheme I-13. Possible reaction pathways of macrocyclic RCM with and without a 2-silyl group (A); route to compound **35** from RCM of the vinylsiloxane (B).



Based on our data, we propose a model for the reaction pathways depicted in Scheme **I-13**, **A**. Several unproductive pathways are involved in RCM reactions of simple olefins including re-opening of the monocyclized product (**A**$^{-}$), CM to generate an acyclic dimer or oligomer (**B**, **C**), and potential cyclization at either of these stages (**C**, **D**). In contrast,

when the silyl group is incorporated in one of the olefins, pathway **A** leading to the desired product is no longer reversible. When we re-subjected the purified trisubstituted silylalkene product to the reaction conditions, no ring-opening product was observed. Pathway **B** exists to generate the acyclic dimers, but only through the CM between the simple olefins – the 2-silyl alkene remains a spectator to CM under our reaction conditions.[239] However, when re-subjected to the reaction conditions, the purified acyclic cross-dimers (*E* and *Z*) of the silylated substrates **13a'** yielded macrocyclic products with 60% ^{1}H NMR yield comparable to that starting from monomer (Scheme **I-14**). Additionally, since the 2-silyl alkene remains a spectator to CM, pathway **C** is shut down. Pathway **D** is also blocked because the formation of a tetrasubstituted alkene with two silyl groups is highly disfavored.

Scheme I-14. RCM of acyclic dimers of **13a'** compared to the reaction with monomer **13a'**.



Overall, the silyl group is able to lower the reactivity of the attached olefin, thereby suppressing non-productive pathways while still allowing the pathways to yield the desired product. In agreement with this analysis, for the substrates that gave low yields, only unreacted starting material, the acyclic cross-dimers, and a styrene derivative were

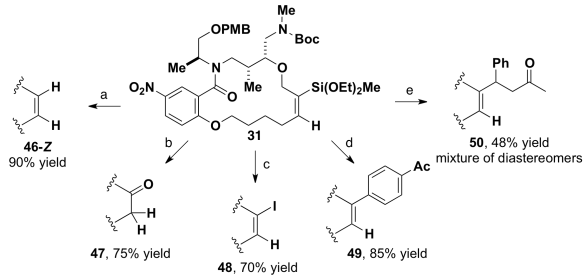
observed along with the product. To explore the "trapping" role of the silyl group, the monocyclized (*Z*)-alkene **35** (not observed from the RCM of the simple olefin substrate **35'**, Scheme **I-13**, **B**) obtained from protodesilylation of compound **16** was subjected to reaction condition II. Not surprisingly, it was almost completely consumed to generate dimers and oligomers. Owing to the fact that the silyl group can be removed, this method offers a means to cyclize some recalcitrant substrates using RCM.

Chapter I-3. Diversification of Alkenylsiloxanes and Alkenylsilanes

1. Further transformation of macrocyclic alkenylsiloxanes

As a principle goal of this project, we aimed to demonstrate the synthetic versatility of alkenylsiloxanes by directly transforming them into a variety of different products (Scheme **I-15**). Alkenyl siloxanes are capable of undergoing a wide range of transformations. Accordingly, the simple *Z*-disubstituted olefin **46-*Z*** was obtained by protodesilylation.[165] This two-step process affords *Z* olefins selectively from RCM reactions. Oxidation of the alkenyl siloxane generated ketone **47** at the carbon bearing the siloxyl group.[244] Ketones, which are found in many biologically active and naturally occurring small molecules, have not typically been obtained from metathesis products in the past except from the RCM product of enol ethers. Our methodology should permit the synthesis of ketones at either of the alkenyl carbons.

Scheme I-15. Further transformation of the alkenyl siloxane **31**.



a) AgF, MeOH/THF, 23 °C, 3 h; b) H_2O_2, KF, $KHCO_3$, MeOH/THF, 23 °C, 3 h; c) I_2, KF, K_2CO_3, DMF, 50 °C, 48h; d) 4'-iodoacetophenone, TBAF, $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), 50 °C, 5h; e) *trans*-4-phenyl-3-buten-2-one, TBAF, $[RhCl(cod)]_2$ (20 mol%).

The direct synthesis of trisubstituted macrocyclic olefins using RCM is generally challenging.[154,161,217,245] The siloxyl-substituted macrocycles provide an effective solution

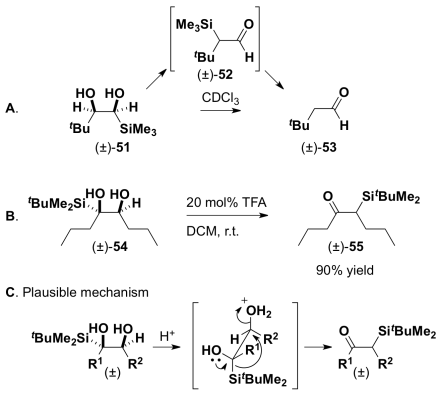
to this synthetic objective. An *ipso*-iodination of the alkenyl siloxane provided alkenyl iodide **48**, a substrate with considerable synthetic potential in transition metal-catalyzed cross-coupling reactions. We also achieved several carbon-carbon bond-forming reactions using the macrocyclic alkenyl siloxane directly. A palladium-catalyzed cross-coupling enabled direct C-C bond formation with an aryl halide, affording the aryl-appended macrocycle **49**.[246] The alkenyl siloxane also underwent a conjugate addition to an α,β-unsaturated ketone in the presence of a rhodium catalyst to generate a C(sp^2)-C(sp^3) bond in compound **50** as a mixture of diastereomers.[247,248]

2. An effective way to synthesize cyclic α-silyl carbonyl compounds via silapinacol rearrangement

Compounds containing α-silyl carbonyl moieties are versatile synthetic intermediates because the silyl group differentiates the two α-positions of a carbonyl moiety that are hard to be selectively transformed otherwise.[249-264] Three conventional ways of accessing the α-silyl carbonyl moiety include α-silylation of carbonyl compounds,[265-268] oxidation of β-silyl alcohols,[269-272] and the addition of silyl-containing organolithium or organomagnesium to esters and acid chlorides.[273-275] It was also reported that α,β-dihydroxysilanes can undergo "silapinacol" rearrangement upon the treatment of an acid to generate α-silyl ketones or aldehydes.[276] Cunico reported that when α,β-dihydroxysilane **51** was dissolved in $CDCl_3$ (without the addition of extra acid), the intermediate α-silyl aldehyde **52** could be observed, coexisting with the starting material for some hours, but slowly collapsing to the desilylated aldehyde product **53** (Scheme **I-16**, **A**). If the appropriate silyl group was selected that is stable at the α position of a

carbonyl moiety under acidic conditions (a TBS group in contrast with a TMS group, Scheme **I-16**, **B**), α-silyl ketones, or aldehydes, can be obtained.

Scheme I-16. Silapinacol rearrangement of acyclic α,β-dihydroxysilanes.

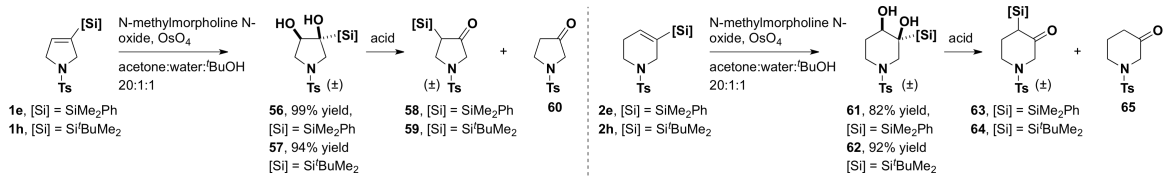


Enabled by the RCM of vinylsilanes and the following *syn*-dihydroxylation catalyzed by OsO_4, cyclic α,β-dihydroxysilanes can be easily accessed. Mr. Miguel Jimenez and I explored the application of the silapinacol rearrangement in these cyclic substrates to obtain cyclic α-silyl ketones that serve as another versatile functionality for further diversification in addition to the direct transformation of vinylsilanes.

Precursors **56**, **57**, **61**, and **62** with two silyl groups were synthesized. Upon treatment of an acid, only the 6-membered ring with a TBS group **62** was able to yield the desired α-silyl ketone **64**. We speculate that the 5-membered ring is not flexible enough to provide the required conformation for the silyl group to migrate (assuming a antiperiplanar relationship between the migrating silyl group and the leaving protonated or borylated β-hydroxy group, Scheme **I-18**, **C**). Unlike the acyclic substrate, 1 equivalent of acid and higher reaction temperatures are required for the rearrangement to occur. Additionally,

stronger acid than TFA is required such as HCl or $BF_3{\cdot}Et_2O$. Finally, the dimethylphenylsilyl group is not stable enough to stay at the α position of ketone.

Table **I-6**. Silapinacol rearrangement of 5- and 6-membered alkenylsilanes under different acids and reaction conditions.



Substrate	Product, yield (conversion)					
	TFA[a]	HCl[b]	$BF_3{\cdot}Et_2O$[c]	$Zn(OTf)_2$[d]	TMSOTf[e]	$MgBr_2$[f]
56	no rxn	**60** 71%	**60** 54%	**60** 37%	**60** (>95%)	no rxn
57	no rxn	**61** 17%	**60** 26%	decomposition	**60** (>95%)	no rxn
61	**65** 24%	**65** 53%	**65** 55%	decomposition	**65** (>95%)	no rxn
62	**64** 20%	**64** 54%	**64** 48%	decomposition	**65** (>95%)	no rxn

[a] Reaction conditions: 1 eq. TFA, 80 °C for substrate **56** and **57**, 50 °C for substrate **61** and **62**, toluene (25 mM), 16 h. [b] Reaction conditions: 1 eq. HCl (1 M solution in Et_2O), 80 °C for substrate **56** and **57**, 50 °C for substrate **61** and **62**, toluene (25 mM), 16 h. [c] Reaction conditions: 1 eq. $BF_3{\cdot}Et_2O$, 50 °C for substrate **56** and **57**, toluene (25 mM); 0 °C for substrate **61** and **62**, DCM (25 mM), 16 h. [d] Reaction conditions: 1.1 eq. $Zn(OTf)_2$, 80 °C for substrate **56** and **57**, 50 °C for substrate **61** and **62**, dioxane (25 mM), 16 h. [e] Reaction conditions: 1 eq. TMSOTf, 0 °C, toluene (25 mM), 2 h. [f] Reaction conditions: 1.2 eq. $MgBr_2$, 80 °C for substrate **56** and **57**, 50 °C for substrate **61** and **62**, toluene (25 mM), 16 h.

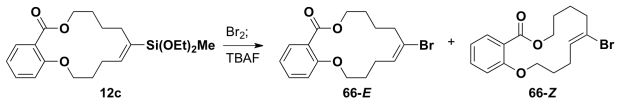
We halted further exploration because we could not access *tert*-butyldimethylsilylalkenes with ring sizes larger than 6 by RCM reaction under our current reaction conditions. Nevertheless, this methodology would greatly increase the diversification potential of the product from RCM of vinylsilanes.

Chapter I-4. Conversion of Macrocyclic (*E*)-Alkenylsiloxanes to the Corresponding (*Z*)-Alkenyl Bromides

Inspired by early studies of Jarvie *et al.*[277] and Miller *et al.*,[278] acyclic alkenylsilanes can be transformed to alkenyl bromides with inversion of stereochemistry. It is desirable to apply this transformation to the macrocyclic alkenylsiloxane obtained from RCM reactions because not only the stereochemistry can be inverted, but the alkenyl bromide also serves as a versatile synthetic intermediate.

Using substrate **12c**, Mr. Miguel Jimenez and I tried some mild dihalogenation reagents such as pyridinium tribromide and phenyltrimethylammonium tribromide. None of them provided complete consumption of starting material or clean reaction without decomposition. We then turned our focus to bromine. Treatment of substrate **12c** in DCM at -78 °C with dropwise addition of bromine solution showed complete consumption of starting material and formation of a dibromide intermediate along with a small amount of alkenyl bromide product suggested by LC-MS analysis. It was found that the dibromide intermediate could convert into the alkenyl bromide on silica gel when running TLC analysis. So instead of isolating the intermediate, a two-step, one-pot procedure was adopted. TBAF was chosen as the bromodesilylation reagent. Upon the addition of up to 4 equivalents of TBAF as solution in THF, the dibromide intermediate completely collapsed to the desired alkenyl bromide after warming up to room temperature. The *E* isomer was assigned by confirming the NOE effect between the two groups of allylic protons. The *Z*:*E* ratio was determined with ^{1}H NMR analysis.

Table I-7. Influence of reaction conditions on the stereoselectivity of converting alkenylsiloxane to alkenyl bromide.



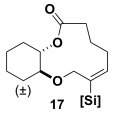
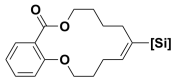
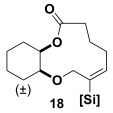
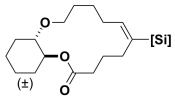
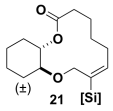
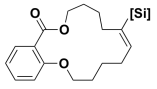
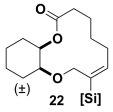
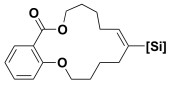
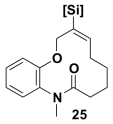
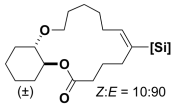
Entry	Solvent	Temp. (°C)	Time[a] (min)	Reaction outcome[b]	Stereoselectivity[c] (*E*:*Z*)
1	DCM	40	5	94%	15:85
2	DCM	0	5	91%	8:92
3	DCM	-78	5	95%	3:97
4	DCM	-100	15	95%	2:98
5	toluene	23	5	94%	17:83
6	toluene	0	5	94%	13:87
7	toluene	-78	5	79%	8:92
8	CS_2	23	5	94%	13:87
9	CS_2	0	5	73%	15:85
10	CS_2	-78	5	95%	3:97
11	THF	23	5	full conv., minor decomp.	31:69
12	THF	0	5	full conv., minor decomp.	22:78
13	THF	-78	5	incompl. conv., minor decomp.	67:33
14	THF	-100	15	incompl. conv., minor decomp.	84:16
15	Et_2O	23	5	>95%[d]	20:80
16	Et_2O	0	5	92%	13:87
17	Et_2O	-78	5	30%	55:45
18	DMF	23	5	incompl. conv., decomp.	n. d.[e]
19	DMF	0	5	incompl. conv., decomp.	n. d.[e]
20	DMF	-78	5	incompl. conv., decomp.	n. d.[e]

[a] Time between addition of Br_2 and TBAF. [b] Isolated yield unless otherwise indicated. [c] Determined by ^{1}H NMR analysis of reaction mixture after workup. [d] Yield determined by ^{1}H NMR analysis. [e] Ratio not determined.

Next we explored the influence of solvent and temperature on the stereoselectivity of this transformation (Table **I-7**). It was found that nonpolar solvents (DCM, CS_2, and toluene) generally favored inversion of stereochemistry leading to the desired (*Z*)-alkenyl bromide. In these solvents, lowering temperature could increase the selectivity towards the *Z* isomer, and reactions could reach complete conversion in most cases. On the

contrary, polar solvent such as DMF favored the retention of stereochemistry yielding the *E* isomer as the major product independent of reaction temperature. Also, side reactions that led to decomposition became significant in DMF. Interestingly, when the reaction was performed in ether or THF, the reaction proceeded slower at lower temperature (-100 °C to -78 °C) with higher *E* selectivity. As temperature was elevated, both the conversion and *Z* selectivity were increased. Reaction mechanisms leading to the formation of either stereoisomers and the role of solvents are not fully clear at this point.

Table I-8. Stereoselectivity of converting (*E*)-alkenylsiloxane substrates to the corresponding alkenyl bromide.

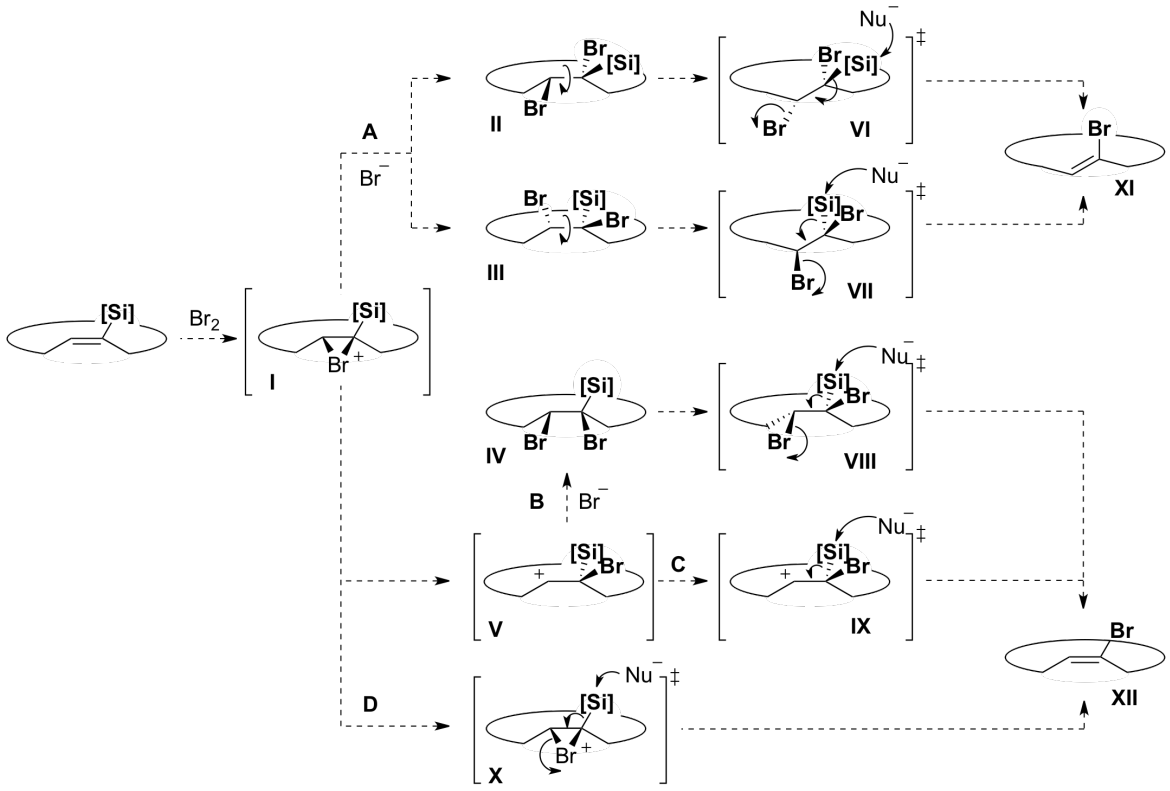
Substrate[a]	Alkenyl bromide, (*E*:*Z*)[b]	Substrate	Alkenyl bromide, (*E*:*Z*)
 17	**67**, 87:13	 12c	**66**, 3:97
 18	**68**, 44:56	 29	**72**, 6:94
 21	**69**, > 98:2	 13c	**73**, 2:98
 22	**70**, 86:14	 27	**74**, 2:98
 25	**71**, > 98:2	 30	**75**, 12:88

[a] [Si] equals diethoxymethylsilyl. [b] Reaction condition: alkenylsiloxane (1 eq.), Br_2 (1.05 eq.), DCM (40 mM), -78 °C, 5 min; TBAF (4 eq.), warmed up to r.t., 15 min. *E*:*Z* ratio was determined by ^{1}H NMR analysis of crude extract.

The stereoselectivity of the product is further complicated by the fact that macrocyclic substrates may have intrinsic conformational constraints that affect stereochemistry of

each step in the reaction sequence. As shown in Table **I-8**, 11- or 12-membered rings gave retention of stereochemistry, while 14- and 15-membered rings yielded almost complete inversion.

Scheme I-17. Proposed reaction mechanism of dibromination/bromodesilylation leading to either stereoisomer.



A general model that explains the dependency of stereochemistry on the ring size of the macrocycle is proposed in Scheme **I-17**. In the ideal situation, once the bromonium ion **I** is formed, the bromide (Br^-) attacks from the back to generate the *anti*-dibromide (pathway **A**). The issue of which carbon the bromide attacks (**II** or **III**) is inconsequential as long as the relative stereochemistry of the dibromide is *anti*. Upon treatment with

TBAF, bromodesilylation happens only when the β-bromo group is antiperiplanar to the silyl group via rotation about the C-C bond (transition state **VI** and **VII**) following an E_2 mechanism. The products from both intermediates are the same (*Z*)-alkenyl bromide (**XI**).

This explains the high selectivity observed for the 14- or 15-membered substrates when reactions are performed in *nonpolar* solvents at low temperature. However at higher temperatures, the *Z* selectivity decreases because the E_2 process is eroded by the E_1 process (pathway **C** via the fully formed carbocation or **D** via rearrangement of the bromonium ion). Additionally, at these temperatures *syn*-dibromination may occur also leading to the *E* product (pathway **B**).

In *polar* solvents the situation is reversed since the solvent can stabilize either the bromonium ion or the fully formed carbocation. When the reaction of substrate **12c** was performed in solvents such as THF or ether, a critical temperature exists, below which pathways leading to the *E* product (**B**, **C**, or **D**) become dominant (observed at -100 °C) potentially because the solvent-stabilized cation does not easily undergo a back-side attack by another bromide; however above this critical temperature pathways leading to the *Z* product (**A**) become dominant (observed at 0 °C) because the desired *anti* dibromide can readily form as with nonpolar solvents but with lower selectivity.

For 11- or 12-membered substrates, pathway **A** becomes disfavored even in nonpolar solvent (Table **I-8**, substrate **17**, **18**, **21**, **22**, and **25**). It is possible that in these smaller

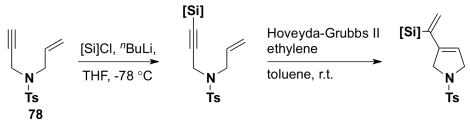
ring-sizes, even though the reactivity of the bromonium ion is maintained, the back side of the bromonium ion is blocked by the backbone and the substituents of the macrocycle transannularly so that *anti*-dibromination is largely prohibited at the temperatures reported. Another possibility is that the (*E*)-alkenyl bromide product is higher in energy than the *Z* isomer. So even if the *anti*-dibromide is initially formed, it may revert to the bromonium ion and eventually form the *Z* product through the pathways mentioned above. Further mechanistic study is warranted to understand the stereoselectivity with different substrates.

Chapter I-5. Applications of the Silyl Group in Other Types of Metathesis Reactions

1. Enyne RCM of alkynylsilanes and alkynylsiloxanes

Mr. Michele Melchiorre and Ms. Cinzia Botta initiated the enyne RCM study. They used a model substrate to show the importance of the silyl groups in the enyne metathesis (Table **I-9**). A number of silyl groups could be installed on the terminal alkyne with moderate to excellent yields. However, three silyl groups (Entry **1**, **2**, and **4**) failed to afford the desired butadiene product under optimized reaction conditions.

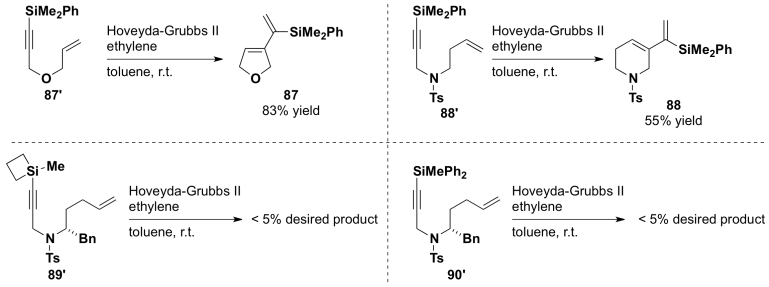
Table I-9. Influence of the silyl group on the enyne RCM reactions.



Entry	[Si]	Silylation Product, Yield (%)	Enyne RCM Product, Yield (%)	Entry	R group	Silylation Product, Yield (%)	Enyne RCM Product, Yield (%)
1	$SiClMe_2$	**79'**, 80	no rxn	**5**	$SiMe_2Ph$	**83'**, 72	**83**, 74
2	$Si(OMe)Me_2$	**80'**, 32	no rxn	**6**	$SiMe_3$	**84'**, 91	**84**, 77
3	$Si(O^tBu)Ph_2$	**81'**, 95	**81**, 49	**7**	$SiBnMe_2$	**85'**, 76	**85**, 93
4	$SiHMe_2$	**82'**, 76	no rxn	**8**	$SiMePh_2$	**86'**, 75	**86**, 96

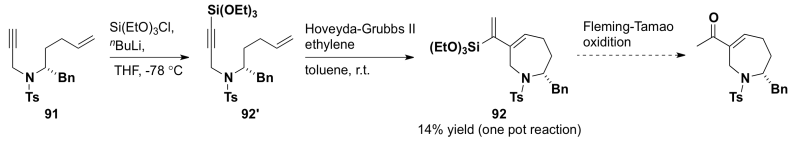
Ms. Cinzia Botta and Mr. Brandon Silverman then studied the generality of the enyne RCM reaction to form different sized products. It was found that when the ring sizes become larger, the yield for the enyne RCM dropped significantly (Scheme **I-18**). Especially substrate **89'** and **90'** failed to generate any detectable amount of 7-membered ring products.

Scheme I-18. Reaction outcome of enyne RCM yielding products with different ring sizes.



Based on the initial study on this reaction and our understanding of the role of silyl groups in the RCM reaction, I explored the reaction to form the 7-membered product using a triethoxysilyl group (Scheme **I-19**). Initial efforts to separate the alkynylsiloxane **92'** failed because it decomposes on silica gel. Instead, a one-pot procedure was adopted. After silylation of the terminal alkyne **91**, the reaction was concentrated and then a solution of Hoveyda-Grubbs second-generation catalyst in toluene was added. The resulting mixture was charged with ethylene gas and left at room temperature for 12 hours. The overall yield of desired silyl-diene **92** after workup and flash chromatography was 14% without any optimization. Further effort is required to find the optimal silyl group that is compatible with the enyne RCM reaction and at the same time suitable for following transformations especially the Fleming-Tamao oxidition.

Scheme I-19. Initial exploration on synthesis and enyne RCM of triethoxysilyl-containing substrate to form a 7-membered product.

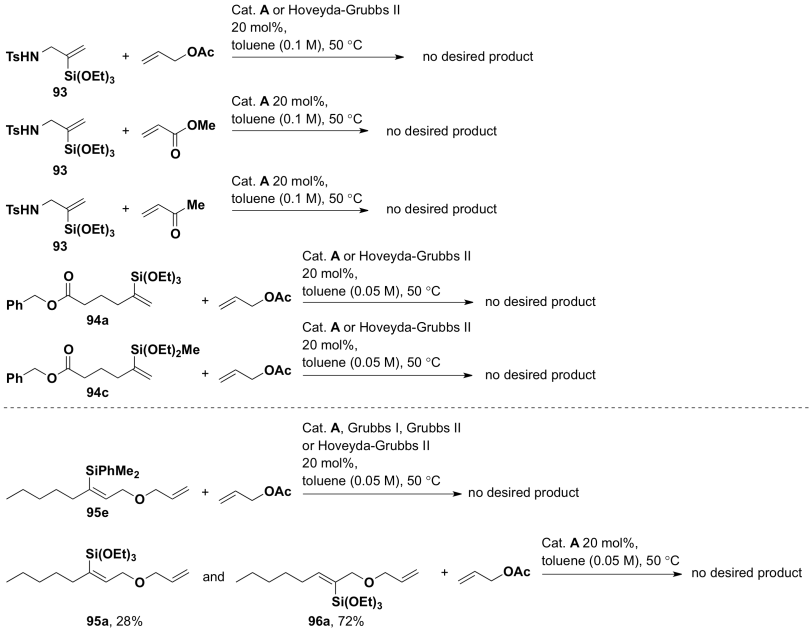


2. Cross metathesis and relay cross metathesis of vinylsiloxanes

In order to understand the role of the silyl group in determining stereochemistry of the macrocyclic RCM reaction, CM of geminal-disubstituted silanes or siloxanes with a monosubstituted olefin was performed. Without any intrinsic preference toward *Z* or *E* imposed by macrocyclic comformation and transannular interactions, the stereoselectivity of the CM reaction would reflect the influence of the sterics of the silyl group. However, we failed to observe any desired product forming in any of the reactions listed in Scheme **I-20**. Difficulties in achieving CM of geminal-disubstituted siloxanes categorized them in the spectator class for CM reaction under current reaction conditions, which is in accordance with our analysis of the reaction pathway mentioned in Chapter **I-2-7**.

In order to overcome the low reactivity of sterically hindered geminal-disubstituted olefins, we have explored a strategy called relay metathesis used in RCM reaction.[279-282] Compound **95e** was synthesized and subjected to the CM reaction with allyl acetate. We failed to observe any desired product under these conditions (Scheme **I-20**). Only homodimers of allyl acetate were observed. The effort to synthesize compound **95a** with a $Si(OEt)_3$ group instead of a $SiPhMe_2$ was more challenging. An inseparable mixture of both regioisomers (**95a** and **96a**) was obtained and the desired isomer is the minor product. Although we did not observe any desired CM product upon treatment of the mixture with catalyst **A** and allyl acetate, the result was inconclusive. Further investigation into the relay CM is warranted.

Scheme I-20. Attempted CM between geminal-disubstituted vinylsiloxanes and a monosubstituted olefin; attempted relay CM reactions.



Chapter I-6. Conclusion and Future Directions

In summary, the introduction of silyl groups into several types of metathesis reactions has been extensively explored. The macrocyclic RCM was the primary focus. Under optimized reaction conditions, a series of 8- to 16-membered macrocyclic rings containing trisubstituted olefins and other useful functionality, including rings having complex substitution patterns, can be accessed. The results demonstrated that the silyl group plays three roles: control of the stereoselectivity of the reaction favoring formation of the *E* product, trapping the desired product by preventing the undesired reaction pathways, and providing the diversification potential with regiochemical control. However, introduction of the silyl group compromises the generality of the RCM reaction to some extent, which is compounded by the instability of the optimal catalyst. Future works on development of metathesis catalyst can be done to increase the generality of this methodology.

In addition, it has been shown that (*E*)-alkenyl siloxanes can be transformed to (*Z*)-alkenyl bromides with inversion of stereochemistry. The alkenyl bromide can also serve as a versatile chemical handle for further diversification. The stereoselectivity of this transformation is substrate-dependent, however, we have not fully understood the reaction mechanism. Both *Z*/*E* isomers of a variety of trisubstituted macrocyclic alkenes are accessible for substrates that give complete inversion of stereochemistry from alkenylsiloxane to alkenyl bromide.

To utilize the diversification potential of the silyl group, enyne RCM of alkynylsiloxanes were studied yielding limited success thus far. Further exploration is required to understand the stability of the alkynylsiloxane, the compatibility of the silyl group in the RCM reaction, the optimal catalyst and reaction conditions, and substrate generality of this reaction.

Attempts to effect a CM between a vinylsiloxane and a simple alkene were made to understand the role of silyl groups in determining stereoselectivity of the RCM reaction. Different substrates and reaction conditions as well as the relay strategy were tried but failed to generate a detectable amount of products. It is likely that novel catalysts will be required for this transformation.

Experimental section

1. Material and Methods

Except as otherwise noted, reactions were carried out under argon. All reaction solvents except acetone and pyridine were dispensed from a solvent purification system wherein solvents are passed through a packed activated alumina column. Acetone was Aldrich 99.5+% histological grade. Pyridine was Aldrich 99.8% histological grade. NMR spectra were recorded at 500 MHz using a Varian I-500 instrument. Chemical shifts for proton NMR spectra are reported in parts per million downfield from tetramethylsilane and were referenced to residual protonated solvent ($CHCl_3$: d 7.26, C_6H_6: d 7.15). Chemical shifts for carbon NMR spectra are reported in parts per million downfield from tetramethylsilane and referenced to protonated solvent ($CHCl_3$: d 77.0, C_6H_6: d 128.0). Data are represented as follows: chemical shift (multiplicity [bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet], coupling constants in Hertz, integration). High-resolution mass spectra were obtained through the Harvard University mass spectrometry facility. Infrared spectra were obtained with a Nicolet IR100 FTIR from Thermo Scientific. Optical rotations were obtained using digital polarimeter Autopol IV (Rudolph research Analytical) with a 1 mL cell and a 1 dm path length. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 precoated plates (0.25 mm). Flash chromatography was performed either with the indicated solvent on E. Merck silica gel 60 (230-400 mesh) or using a CombiFlash companion system (Teledyne ISCO, Inc.) with pre-packed FLASH silica gel columns (Teledyne ISCO, Inc.). SFC/MS chromatography was performed with a Berger analytic SFC (Waters ZQ Mass Spectometer) using CO_2 and isopropanol as the

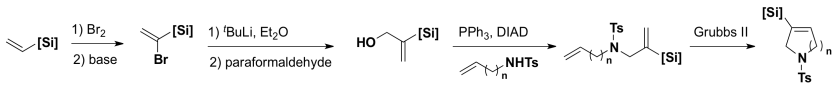
mobile phase and using a Chiralpak® AD-H column purchased from Chiral Technology Inc. (column length: 4.6x250mm, particle size: 5um). HPLC purification was performed on a Waters mass-directed autopurification system. The system consisted of 2767 injection/collection sample manager, a 2525 binary gradient high pressure LC pump, two 515 pumps to deliver makeup and dilution flow, a column fluidic organizer (CFO), a 2996 photodiode array detector, and a ZQ quadropole MS equipped with an electrospray interface. All of the instrumentation was controlled by MassLynx and FractionLynx software versions 4.1. All reagents were obtained from commercial sources and used without further purification.

2. Experimental procedures

Note on compound numbering: ring-closed products are designated as the parent compound and numerated with just a number with or without a letter. Whenever necessary, *Z* or *E* is used to distinguish between both stereoisomers. Substrates (simple, silyl-containing, or enyne) for RCM reactions are designated with a prime after the compound name. The undesired regioisomer of the vinylsiloxane from the hydrosilylation reaction is designated with double primes after the name. The styrene derivative from the RCM reaction is labeled with 's' after the name of the substrate. For the same scaffold that has different silyl groups, letters are used to differentiate: 'a' $Si(OEt)_3$; 'b' $Si(OEt)_2Ph$; 'c' $Si(OEt)_2Me$; 'd' $Si(OEt)Me_2$; 'e' $SiMe_2Ph$; 'f' $SiEt_3$; 'g' $SiMe_3$; 'h' Si^tBuMe_2.

A. Synthesis and RCM of vinylsilane

Scheme I-21. Synthetic route toward cyclic alkenylsilanes.



As shown in Scheme **I-21**, it takes three steps to access the silyl-containing diolefinic substrates for RCM reactions. According to the literature,[283] the first step involves a dibromination and HBr elimination of a vinylsilane to generate the bromovinylsilane. The second step starts with a lithium-bromo exchange of the bromovinylsilane, which is subsequently quenched with paraformaldehyde. Then the allyl alcohol is subjected to a Mitsunobu reaction with tosylamine serving as a nucleophile. The general procedures of these three steps are described as follows.

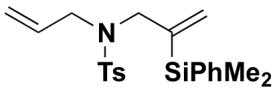
Bromine (1 equiv.) in carbon tetrachloride (1.2 M) was added dropwise, via a cannula, to a stirred solution of vinylsilane (1 equiv.) in carbon tetrachloride (1.2 M) at 0 °C. The solution was stirred for 10 min at 0 °C, washed sequentially with saturated aqueous sodium hydrogen carbonate containing some sodium hydrogen sulfite (3 × 50 ml) and brine (50 ml), dried over magnesium sulfate and concentrated *in vacuo* to give the crude dibromide. This crude product was dissolved in diethylamine (0.6 M) and refluxed for 12 h. After cooling to room temperature, the dark brown reaction mixture was diluted with diethyl ether and washed with water. The organics were then washed with brine, dried over sodium sulfate and concentrated *in vacuo*, which was then purified by flash column chromatography (hexane) to give the bromovinylsilane.

To a stirred solution of bromovinylsilane in diethyl ether (0.3 M) at -78 °C, *tert*-butyllithium (1.7 M solution in pentane, 2.1 equiv.) was added dropwise. After complete addition, the reaction was stirred for 1 h at -78 °C. A solution of paraformaldehyde (2 equiv.) in diethyl ether (2.5 M) was then added dropwise via a cannula. After stirring for 1 hour at -78 °C, the reaction was allowed to warm to room temperature. Water was added, the mixture was separated and the aqueous layer was extracted with diethyl ether for 3 times. The organics were then washed with brine, dried over sodium sulfate and concentrated *in vacuo*, which was purified by flash column chromatography (5% ethyl acetate in hexane) to give the vinylsilane-containing alcohol.

The vinylsilane-containing alcohol was dissolved in THF (0.1 M). PPh_3 (1.2 equiv.) was added to the solution. Then N-alkenyl-4-methylbenzenesulfonamide (1.1 equiv.) was added. The reaction was cooled to 0 °C. DIAD (1.1 equiv.) was added dropwise. The reaction was warmed to r.t. and stirred for 12h. The reaction mixture was concentrated *in vacuo*. The residue was purified via flash column chromatography (10% ethyl acetate in hexane) to give the RCM substrate.

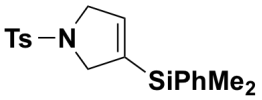
Initial RCM reaction conditions: substrate (1 equiv.) was dissolved in anhydrous DCM at a concentration of 20 mM (for compound **1e'** and **2e'**) or 3 mM (for compound **1h'**, **2h'**, **3e'**, **3h'**, **4a'**, **5'**, **11a'**, and **11b'**) under argon. Grubbs II (10 mol% for **1e'** and **2e'**; 20 mol% for others) was added to the solution. The reaction was kept at room temperature for 18 hours (for **1e'** and **2e'**) or heated up to 40 °C for 18 hours (for other substrates). The resulting mixture was concentrated under reduced pressure and the residue was

analyzed by ^{1}H NMR or purified by silica gel column chromatography using Hexanes/EtOAc as eluent.



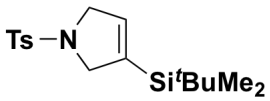
***N*-allyl-*N*-(2-(dimethyl(phenyl)silyl)allyl)-4-methylbenzenesulfonamide (1e')**

Yield 46% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.66-7.64 (m, 2 H), 7.61-7.49 (m, 2 H), 7.37-7.33 (m, 3 H), 7.27-7.25 (m, 2 H), 5.83-5.82 (m, 1 H), 5.54-5.53 (m, 1 H), 5.39-5.30 (m, 1 H), 4.96-4.94 (m, 1 H), 4.90-4.86 (m, 1 H), 3.83 (s, 2 H), 3.66 (d, J = 7.0 Hz, 2 H), 2.41 (s, 3 H), 0.41 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.1,143.0, 137.3 137.1, 133.9, 132.0, 129.6, 129.2, 128.1, 127.8, 127.2, 119.3, 51.0, 49.6, 21.5, -3.4.



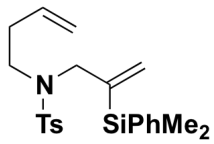
3-(dimethyl(phenyl)silyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1e)

Yield 92% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.5 Hz, 2 H), 7.39-7.26 (m, 7 H), 5.82 (t, J = 1.0 Hz, 1 H), 4.17-4.13 (m, 4 H), 2.43 (s, 3 H), 0.33 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.3, 138.9, 136.2, 135.3, 134.4, 133.6, 129.7, 129.5, 127.9, 127.3, 58.5, 56.6, 21.5, -3.4.



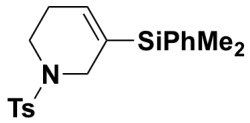
3-(*tert*-butyldimethylsilyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (1h)

Yield 86% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 5.78 (t, *J* = 1.3 Hz, 1 H), 4.20-4.18 (m, 2 H), 4.14-4.12 (m, 2 H), 2.42 (s, 3 H), 0.80 (s, 9 H), 0.01 (s, 6 H; ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.3, 138.4, 135.1, 134.4, 129.7, 127.3, 59.4, 56.5, 26.3, 21.5, 16.6, -6.4.



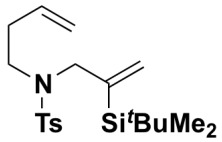
***N*-(but-3-en-1-yl)-*N*-(2-(dimethyl(phenyl)silyl)allyl)-4-methylbenzenesulfonamide (2e')**

Yield 69% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2 H), 7.52-7.50 (m, 2 H), 7.38-7.26 (m, 3 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 5.85-5.84 (m, 1 H), 5.55-5.47 (m, 2 H), 4.92-4.85 (m, 2 H), 3.83 (s, 2 H), 3.06-3.03 (m, 2 H), 3.41 (s, 3 H), 2.02-1.98 (m, 2 H), 0.43 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.5, 143.0, 137.1, 137.0, 134.7, 133.9, 129.6, 129.3, 128.2, 127.9, 127.1, 116.7, 52.3, 47.1, 32.1, 21.5, -3.4.



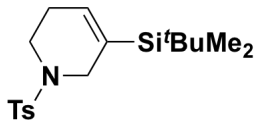
5-(dimethyl(phenyl)silyl)-1-tosyl-1,2,3,6-tetrahydropyridine (2e)

Yield 82% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 6.0 Hz, 2 H), 7.45-7.43 (m, 2 H), 7.39-7.32 (m, 3 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 6.03-6.01 (m, 1 H), 3.62-3.61 (m, 2 H), 3.16 (t, *J* = 6.0 Hz, 2 H), 2.42 (s, 3 H), 2.25-2.22 (m, 2 H), 0.33 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.3, 136.7, 135.0, 133.8, 133.7, 133.5, 129.5, 129.2, 127.8, 127.5, 46.4, 42.2, 26.6, 21.4, -3.6.



***N*-(but-3-en-1-yl)-*N*-(2-(*tert*-butyldimethylsilyl)allyl)-4-methylbenzenesulfonamide (2h')**

Yield 76% (colorless oil); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.3, 143.0, 137.3, 134.7, 129.6, 127.4, 127.1, 116.9, 53.2, 47.5, 32.7, 26.7, 21.5, 16.9, -6.2.

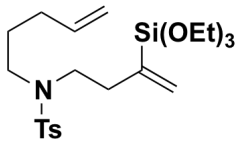


5-(*tert*-Butyldimethylsilyl)-1-tosyl-1,2,3,6-tetrahydropyridine (2h)

Yield 18% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.5 Hz, 2 H), 7.31 (d, J = 8.5 Hz, 2 H), 5.99-5.97 (m, 1 H), 3.63 (dt, J = 2.3, 2.3 Hz, 2 H), 3.15 (t, J = 5.5 Hz, 2 H), 2.43 (s, 3 H), 2.28-2.24 (m, 2 H), 0.84 (s, 9 H), 0.02 (s, 6 H).

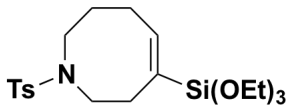
B. Initial synthesis and RCM of vinylsiloxane

Hydrosilylation: following the literature procedure,[197,198] to a solution of the alkyne substrate (1 equiv.) in DCM (0.5 M) was added the diethoxymethylsilane (1.1 equiv.). The flask was cooled to 0 °C and catalyst [Cp*Ru(MeCN)$_3$]PF$_6$ (5 mol%) was added. The ice bath was immediately removed and the solution was stirred for 30 min. The resulting mixture was concentrated *in vacuo* and the residue was purified by silica gel column chromatography using Hexanes/EtOAc as eluent to give the RCM substrate.



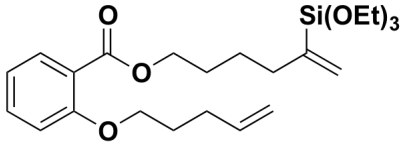
4-methyl-*N*-(pent-4-en-1-yl)-*N*-(3-(triethoxysilyl)but-3-en-1-yl)benzenesulfonamide (4a')

Yield 68% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 5.81-5.73 (m, 2 H), 5.67-5.66 (m, 2 H), 5.03-4.99 (m, 2 H), 4.98-4.96 (m, 2 H), 3.83-3.78 (m, 6 H), 3.23-3.20 (m, 2 H), 3.14 (t, *J* = 7.6 Hz, 2 H), 2.41 (s, 3 H), 2.37-2.33 (m, 2 H), 2.05 (dt, *J* = 7.0, 7.0 Hz, 2 H), 1.69-1.63 (m, 2 H), 1.23-1.20 (m, 9 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.9, 140.2, 137.5, 137.2, 131.7, 129.5, 127.1, 115.2, 58.6, 48.0, 47.9, 35.6, 30.8, 27.7, 21.5, 18.2.



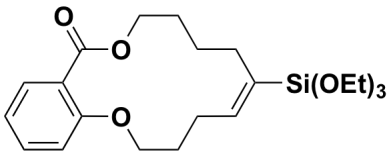
(*E*)-1-tosyl-6-(triethoxysilyl)-1,2,3,4,7,8-hexahydroazocine (4a)

Yield 71% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2 H), 7.28 (d, *J* = 8.5 Hz, 2 H), 6.37 (t, *J* = 8.2 Hz, 1 H), 3.82-3.75 (m, 6 H), 3.16 (bs, 2 H), 3.04-3.02 (m, 2 H), 2.44-2.30 (m, 7 H), 1.79-1.75 (m, 2 H), 1.21-1.18 (m, 9 H).



5-(Triethoxysilyl)hex-5-en-1-yl 2-(pent-4-en-1-yloxy)benzoate (12a')

Yield 72% (colorless oil); IR (neat, cm^{-1}) 3077, 2974, 2927, 2890, 2736, 1729, 1705, 1641, 1601, 1583, 1492, 1469, 1452, 1390, 1301, 1251, 1165, 1080, 1016, 958; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1 H), 7.44-7.40 (m, 1 H), 6.97-6.93 (m, 2 H), 5.85 (ddt, *J* = 17.0, 10.5, 6.8 Hz, 1 H), 5.74-5.73 (m, 1 H), 5.65-5.65 (m, 1 H), 5.08-5.04 (m, 1 H), 4.99 (d, *J* = 10.0 Hz, 1 H), 4.30 (t, *J* = 6.8 Hz, 2 H), 4.04 (t, *J* = 6.5 Hz, 2 H), 3.82 (q, *J* = 6.8 Hz, 6 H), 2.28 (dt, *J* = 7.2, 7.2 Hz, 2 H), 2.21 (t, *J* = 7.8 Hz, 2 H), 1.93 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.76 (tt, *J* = 7.2, 7.2 Hz, 2 H), 1.65-1.59 (m, 2 H), 1.22 (t, *J* = 6.5 Hz, 9 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.5, 143.3, 137.7, 133.1, 131.5, 129.4, 120.1, 120.0, 115.2, 113.1, 68.0, 64.8, 58.5, 35.6, 30.0, 28.5, 28.3, 25.1, 18.2; HRMS (ESI-TOF) calcd. for $C_{24}H_{38}O_6Si$ $[M+Na]^+$ 473.23299, found 473.23204.



(*E*)-6-(triethoxysilyl)-3,4,7,8,9,10-hexahydrobenzo[*b*][1,5]dioxacyclotetradecin-12(2*H*)-one (12a)

Yield 92% (pale yellow oil) with optimized reaction conditions; IR (neat, cm^{-1}) 3076, 2972, 2927, 2735, 1705, 1602, 1582, 1491, 1453, 1387, 1302, 1252, 1166, 1128, 1080, 1025, 996, 958; ^{1}H-NMR (500 MHz, C_6D_6) δ 7.79-7.77 (m, 1 H), 7.44-7.41 (m, 1 H), 6.97 (dd, *J* = 7.5, 7.5 Hz, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 6.21 (t, *J* = 8.0 Hz, 1 H), 4.43 (t, *J* = 5.2 Hz, 2 H), 4.06 (t, *J* = 5.0 Hz, 2 H), 3.83 (q, *J* = 7.0 Hz, 6 H), 2.43-2.38 (m, 2 H), 2.23-2.19 (m, 2 H), 1.90-1.85 (m, 2 H), 1.83-1.78 (m, 2 H), 1.71-1.65 (m, 2 H), 1.24 (t, *J* = 6.8 Hz, 9 H); ^{13}C-NMR (125 MHz, C_6D_6) δ 168.1, 158.1, 145.2, 134.1, 132.9,

132.8, 122.1, 120.1, 112.1, 67.0, 63.5, 58.6, 30.1, 28.6, 27.7, 26.0, 25.5, 18.6; HRMS (ESI-TOF) calcd. for $C_{22}H_{34}O_6Si$ $[M+Na]^+$ 445.20169, found 445.20168.

C. Catalysts screening

To a round-bottomed flask equipped with magnetic stir bar and armed with a condenser was added substrate **13a'** (1.0 equiv.) in anhydrous dichloromethane (2 mM) under argon. The catalyst (0.2 equiv.) was then added and the reaction was refluxed for 18 hours. The mixture was cooled to room temperature, concentrated under reduced pressure. The conversion was analyzed by crude proton NMR study using $CDCl_3$ as solvent (Table **I-10**). Representative NMR spectrum (olefinic proton area) of the RCM reaction of substrate **13a'** with catalyst **A** was shown in **Figure I-3**. The peak at 6.23 ppm (t) was the resonance of olefin proton within product **13a** (the overlap of product peak with one of the styrene olefin proton was corrected by subtracting integration of the other styrene olefin proton (6.42-6.39 ppm) from the integration of 6.26-6.20 ppm). Unreacted starting material, acyclic cross-dimmers, and the styrene derivative share the common moiety of vinylsiloxane which gives two terminal olefin proton peaks at 5.73 and 5.65 ppm. Integration for one of them and the corrected integration of desired product were then used for determination of the conversion of the reaction. After catalyst **A** was discovered, reaction conditions for RCM of substrate **13a'** were then optimized (see Table **I-3** in Chapter **I-2-2**).

Table I-10. Conversion of the RCM reaction of substrate **13a'** with various catalysts to desired product.

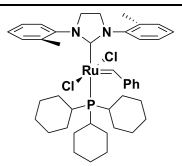
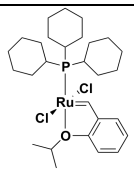
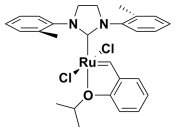
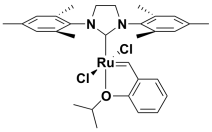
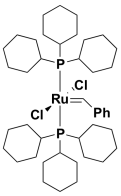
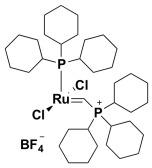
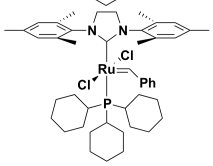
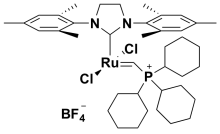
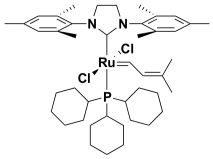
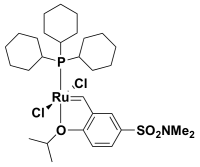
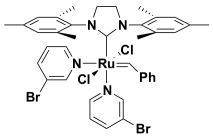
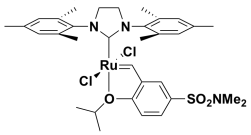
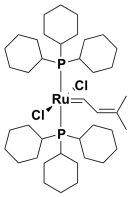
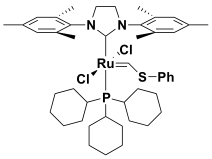
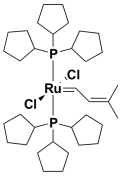
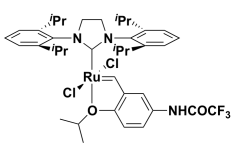
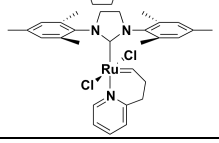
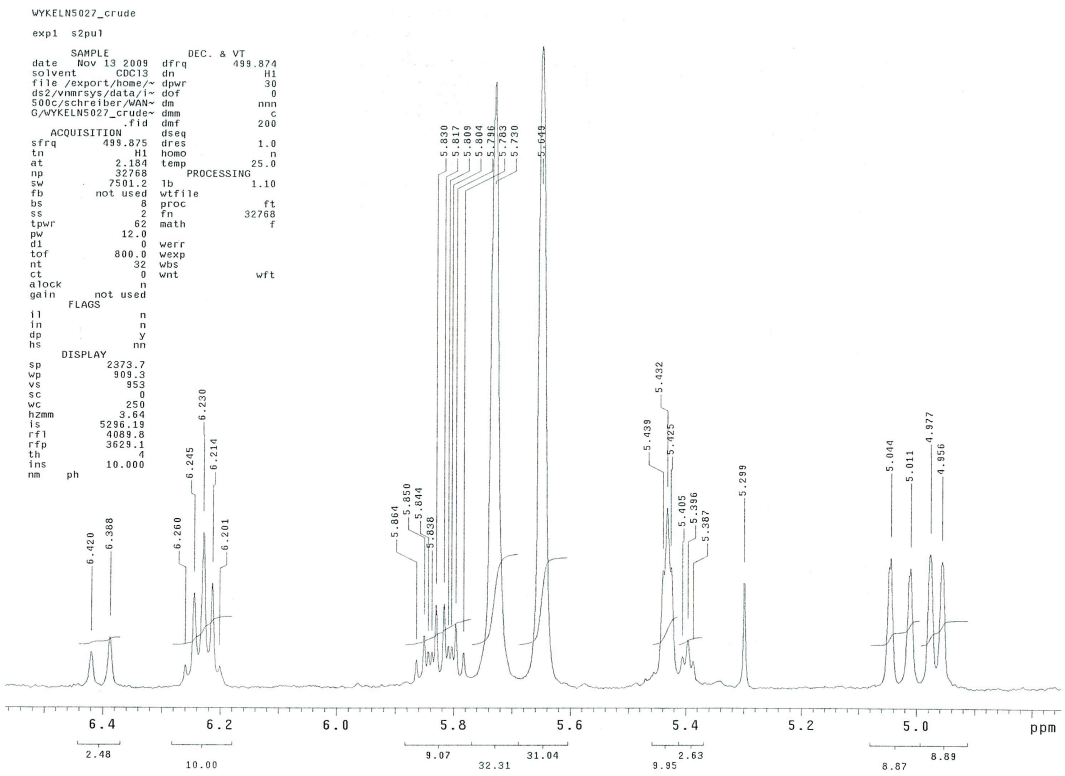
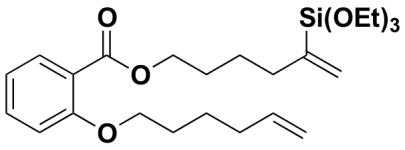
Entry	Catalyst	Conversion to product (%)	Entry	Catalyst	Conversion to product (%)
A		19	**J**		< 2
B		3	**K**		< 2
C		< 2	**L**		< 2
D		< 2	**M**		< 2
E		< 2	**N**		< 2
F		< 2	**O**		< 2
G		< 2	**P**		< 2
H		< 2	**Q**		< 2
I		< 2			

Figure I-3. Representative crude proton NMR spectrum (olefinic proton area) of RCM reaction for catalysts screening, reaction condition optimization, and catalyst decomposition studies.



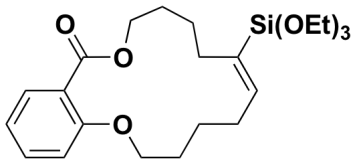
Reaction condition: substrate **13a'** with catalyst **A**, DCM, reflux, 18 hours.

Optimized reaction conditions for RCM of vinyl siloxane substrates: substrate (1 equiv.) was dissolved in anhydrous toluene (or other solvent when indicated) at a concentration of 2 mM under argon. Catalyst **A** (20 mol%) was added to the solution. High vacuum was applied to the reaction flask for 5 min and charged with argon. This operation cycle was repeated for 5 times. The reaction was then heated up to 35 °C and left for 12 hours. The resulting mixture was concentrated under reduced pressure and the residue was analyzed by ^{1}H NMR or purified by silica gel column chromatography using Hexanes/EtOAc as eluent.



5-(Triethoxysilyl)hex-5-en-1-yl 2-(hex-5-en-1-yloxy)benzoate (13a')

Yield 72% (colorless oil); IR (neat, cm^{-1}) 3076, 2974, 2929, 2736, 1729, 1705, 1641, 1601, 1583, 1491, 1452, 1389, 1301, 1249, 1165, 1079, 995, 958; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.44-7.40 (m, 1 H), 6.96-6.93 (m, 2 H), 5.82 (ddt, *J* = 17.0, 10.5, 6.5 Hz, 1 H), 5.73-5.73 (m, 1 H), 5.65-5.65 (m, 1 H), 5.05-5.01 (m, 1 H), 4.97 (d, *J* = 10.5 Hz, 1 H), 4.30 (t, *J* = 6.8 Hz, 2 H), 4.03 (t, *J* = 6.2 Hz, 2 H), 3.82 (q, *J* = 6.8 Hz, 6 H), 2.21 (t, *J* = 7.5 Hz, 2 H), 2.13 (dt, *J* = 7.2, 7.2 Hz, 2 H), 1.84 (tt, *J* = 7.1, 7.1 Hz, 2 H), 1.76 (tt, *J* = 7.1, 7.1 Hz, 2 H), 1.64-1.57 (m, 4 H), 1.22 (t, *J* = 7.0 Hz, 9 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.5, 143.3, 138.5, 133.1, 131.5, 129.4, 120.9, 119.9, 114.7, 113.0, 68.6, 64.8, 58.5, 35.5, 33.4, 28.6, 28.4, 25.2, 25.1, 18.2; HRMS (ESI-TOF) calcd. for $C_{25}H_{40}O_6Si$ $[M+Na]^+$ 487.24864, found 487.24889.



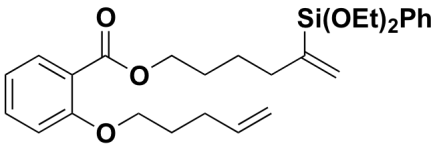
(*E*)-7-(Triethoxysilyl)-4,5,8,9,10,11-hexahydro-2*H*-benzo[*b*][1,5]dioxacyclopentadecin-13(3*H*)-one (13a)

Yield 60% (pale yellow oil) with optimized reaction conditions; IR (neat, cm^{-1}) 2972, 2927, 1700, 1602, 1491, 1453, 1388, 1302, 1250, 1166, 1102, 1078, 1018, 958; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.75-7.74 (m, 1 H), 7.42-7.39 (m, 1 H), 6.96 (dd, *J* = 7.5, 7.5 Hz, 1

H), 6.91 (d, *J* = 8.5 Hz, 1 H), 6.23 (t, *J* = 7.5 Hz, 1 H), 4.40 (t, *J* = 5.5 Hz, 2 H), 4.07 (t, *J* = 5.0 Hz, 2 H), 3.80 (q, *J* = 6.8 Hz, 6 H), 2.27-2.21 (m, 4 H), 1.87-1.77 (m, 4 H), 1.68-1.58 (m, 4 H), 1.22 (t, *J* = 6.8 Hz, 9 H); ^{13}C-NMR (125 MHz, C_6D_6) δ 167.8, 158.2, 145.0, 134.9, 132.6, 132.2, 122.3, 120.1, 112.4, 68.1, 64.3, 58.6, 29.1, 28.9, 28.9, 28.7, 27.1, 26.9, 18.5; HRMS (ESI-TOF) calcd. for $C_{23}H_{36}O_6Si$ $[M+Na]^+$ 459.21734, found 459.21736.

D. Study of influence of silyl groups

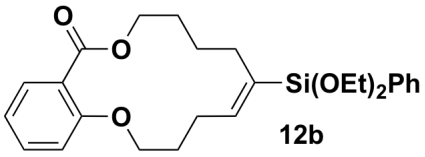
Different vinyl silane or vinyl siloxane substrates were synthesized following general procedure for hydrosilylation using the respective silanes. The RCM reaction was then performed following the general procedure for RCM.



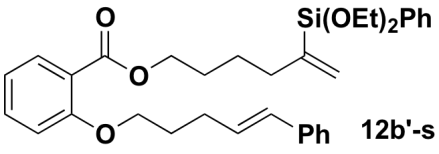
5-(Diethoxy(phenyl)silyl)hex-5-en-1-yl 2-(pent-4-en-1-yloxy)benzoate (12b')

Yield 91% (colorless oil); IR (neat, cm^{-1}) 3071, 2973, 2940, 2881, 1728, 1704, 1641, 1601, 1583, 1491, 1469, 1452, 1430, 1389, 1301, 1251, 1164, 1119, 1101, 1079, 1016, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.76-7.74 (m, 1 H), 7.64-7.62 (m, 2 H), 7.44-7.33 (m, 4 H), 6.96-6.93 (m, 2 H), 5.88-5.79 (m, 2 H), 5.67-5.66 (m, 1 H), 5.06-5.03 (m, 1 H), 4.98 (d, *J* = 10.0 Hz, 1 H), 4.23 (t, *J* = 6.5 Hz, 2 H), 4.03 (t, *J* = 6.5 Hz, 2 H), 3.81 (q, *J* = 7.0 Hz, 4 H), 2.26 (dt, *J* = 7.2, 7.2 Hz, 2 H), 2.22 (t, *J* = 8.0 Hz, 2 H), 1.91 (tt, *J* = 6.9, 6.9 Hz, 2 H), 1.70 (tt, *J* = 7.2, 7.2 Hz, 2 H), 1.56 (tt, *J* = 7.6, 7.6 Hz, 2 H), 1.23 (t, *J* = 7.2 Hz, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.4, 145.5, 137.7, 134.6, 133.3, 133.1,

131.5, 130.0, 129.4, 127.7, 120.8, 120.0, 115.2, 113.1, 68.0, 64.8, 58.7, 35.2, 30.0, 28.4, 28.3, 25.1, 18.3; HRMS (ESI-TOF) calcd. for $C_{28}H_{38}O_5Si$ $[M+Na]^+$ 505.23807, found 505.24127.

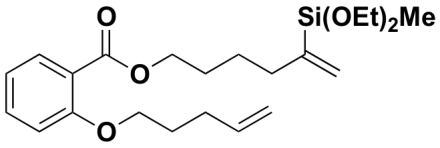


12b and



12b'-s

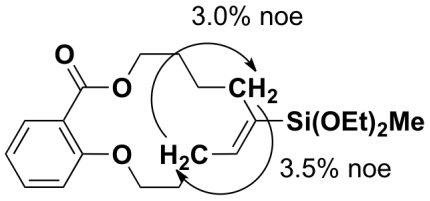
RCM reaction of compound **12b'** gave rise to an inseparable mixture of product **12b** and styrene derivative **12b'-s** as well as acyclic dimer and unreacted starting material. The NMR yield was calculated to be 69% based on analysis of crude ^{1}H NMR spectrum.



5-(Diethoxy(methyl)silyl)hex-5-en-1-yl 2-(pent-4-en-1-yloxy)benzoate (12c')

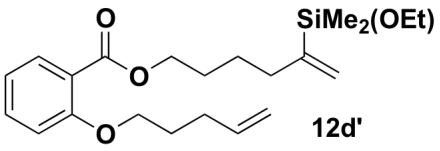
Yield 85% (colorless oil); IR (neat, cm^{-1}) 3077, 2972, 2943, 2879, 2763, 2735, 1728, 1705, 1641, 1601, 1583, 1491, 1452, 1389, 1301, 1253, 1164, 1130, 1103, 1079, 1016, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.0 Hz, 1 H), 7.42 (dd, *J* = 7.2, 7.2 Hz, 1 H), 6.97-6.93 (m, 2 H), 5.85 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H), 5.69 (bs, 1 H), 5.57-5.56 (m, 1 H), 5.06 (d, *J* = 17.5 Hz, 1 H), 4.99 (d, *J* = 10.0 Hz, 1 H), 4.30 (t, *J* = 6.5 Hz, 2 H), 4.04 (t, *J* = 6.5 Hz, 2 H), 3.76 (q, *J* = 6.8 Hz, 4 H), 2.27 (dt, *J* = 7.0, 7.0 Hz, 2 H), 2.21 (t, *J* = 7.5 Hz, 2 H), 1.93 (tt, *J* = 6.9, 6.9 Hz, 2 H), 1.76 (tt, *J* = 7.2, 7.2 Hz, 2 H), 1.60 (tt, *J* = 7.6, 7.6 Hz, 2 H), 1.21 (t, *J* = 7.0 Hz, 6 H), 0.19 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.4, 147.0, 137.7, 133.1, 131.5, 127.7, 120.8, 120.0, 115.2, 113.0, 67.9, 64.8,

58.2, 35.1, 30.0, 28.5, 28.3, 25.1, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{23}H_{36}O_5Si$ $[M+H]^+$ 421.24048, found 421.24067.

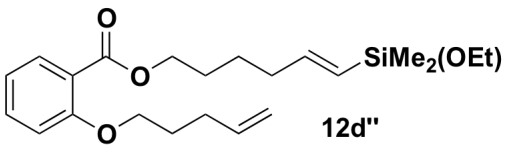


(*E*)-6-(Diethoxy(methyl)silyl)-3,4,7,8,9,10-hexahydrobenzo[*b*][1,5]dioxacyclotetradecin-12(2*H*)-one (12c)

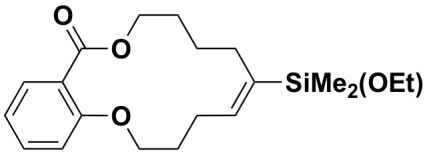
Yield 95% (pale yellow oil); IR (neat, cm^{-1}) 3076, 2970, 2927, 2873, 1705, 1602, 1582, 1491, 1453, 1386, 1356, 1303, 1253, 1165, 1129, 1103, 1079, 1051, 1024, 995; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.79-7.77 (m, 1 H), 7.44-7.41 (m, 1 H), 6.97 (dd, *J* = 7.2, 7.2 Hz, 1 H), 6.92 (d, *J* = 8.0 Hz, 1 H), 6.11 (t, *J* = 8.0 Hz, 1 H), 4.43 (t, *J* = 5.2 Hz, 2 H), 4.06 (t, *J* = 5.0 Hz, 2 H), 3.77 (q, *J* = 7.0 Hz, 4 H), 2.40 (dt, *J* = 6.0, 6.0 Hz, 2 H), 2.21-2.18 (m, 2 H), 1.90-1.84 (m, 2 H), 1.83-1.78 (m, 2H), 1.69-1.62 (m, 2 H), 1.23 (t, *J* = 7.2 Hz, 6 H), 0.19 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.5, 157.6, 143.5, 136.8, 133.1, 132.2, 121.1, 120.1, 112.0, 67.4, 63.8, 58.2, 29.9, 28.4, 26.9, 25.7, 25.3, 18.3, -4.9; HRMS (ESI-TOF) calcd. for $C_{21}H_{32}O_5Si$ $[M+H]^+$ 393.20918, found 393.20943.



and

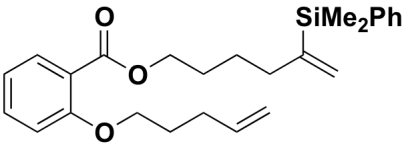


Hydrosilylation reaction gave rise to a 14.4:1 mixture of two regioisomers with the desired regioisomer **12d'** being the major one. Yield 84% (colorless oil).



(*E*)-6-(Ethoxydimethylsilyl)-3,4,7,8,9,10-hexahydrobenzo[*b*][1,5]dioxacyclotetradecin-12(2*H*)-one (12d)

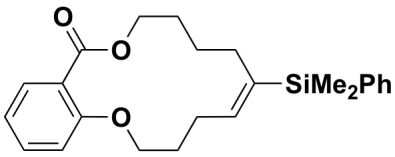
Yield 81% (pale yellow oil); IR (neat, cm^{-1}) 2959, 2926, 2865, 1704, 1602, 1491, 1453, 1386, 1303, 1250, 1164, 1131, 1102, 1080, 1049, 1023, 993; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.79-7.77 (m, 1 H), 7.44-7.41 (m, 1 H), 6.97 (dd, *J* = 7.5, 7.5 Hz, 1 H), 6.92 (d, *J* = 8.5 Hz, 1 H), 5.97 (t, *J* = 8.0 Hz, 1 H), 4.43 (t, *J* = 5.2 Hz, 2 H), 4.06 (t, *J* = 5.0 Hz, 2 H), 3.65 (q, *J* = 7.0 Hz, 2 H), 2.42-2.36 (m, 2 H), 2.22-2.18 (m, 2 H), 1.89-1.84 (m, 2 H), 1.83-1.78 (m, 2 H), 1.67-1.61 (m, 2 H), 1.19 (t, *J* = 7.0 Hz, 3 H), 0.19 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.5, 157.7, 141.7, 139.8, 133.1, 132.3, 121.1, 120.1, 112.1, 67.5, 63.8, 58.4, 30.1, 28.5, 27.2, 25.8, 25.5, 18.5, -2.4; HRMS (ESI-TOF) calcd. for $C_{20}H_{30}O_4Si$ $[M+Na]^+$ 385.18056, found 385.19580.



5-(Dimethyl(phenyl)silyl)hex-5-en-1-yl 2-(pent-4-en-1-yloxy)benzoate (12e')

Yield 93% (colorless oil); IR (neat, cm^{-1}) 3069, 2949, 1728, 1641, 1601, 1491, 1452, 1430, 1387, 1302, 1251, 1164, 1133, 1078, 1050, 1015; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1 H), 7.51-7.49 (m, 2 H), 7.44-7.40 (m,1 H), 7.34-7.32 (m, 3 H), 6.97-6.93 (m, 2 H), 5.84 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1 H), 5.70-5.69 (m, 1 H), 5.42-5.42 (m, 1 H),

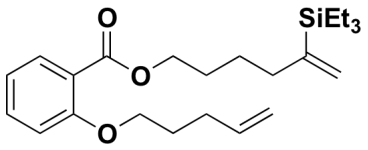
5.06-5.03 (m, 1 H), 4.99 (d, J = 10.5 Hz, 1 H), 4.21 (t, J = 7.0 Hz, 2 H), 4.03 (t, J = 6.5 Hz, 2 H), 2.26 (dt, J = 7.2, 7.2 Hz, 2 H), 2.17 (t, J = 7.5 Hz, 2 H), 1.91 (tt, J = 6.9, 6.9 Hz, 2 H), 1.68 (tt, J = 7.1, 7.1 Hz, 2 H), 1.52-1.46 (m, 2 H), 0.36 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.4, 149.8, 138.2, 137.7, 133.8, 133.1, 131.5, 128.9, 127.7, 126.0, 120.8, 120.0, 115.2, 113.0, 67.9, 64.7, 35.4, 30.0, 28.4, 28.3, 25.1, -3.0; HRMS (ESI-TOF) calcd. for $C_{26}H_{34}O_3Si$ $[M+H]^+$ 423.23500, found 423.23601.



(*E*)-6-(Dimethyl(phenyl)silyl)-3,4,7,8,9,10-hexahydrobenzo[*b*][1,5]dioxacyclotetradecin-12(2*H*)-one (12e)

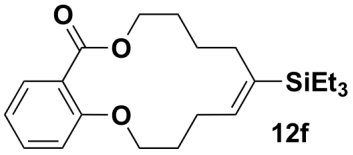
RCM reaction of the previous compound (**18e'**) gave rise to an inseparable mixture of product and styrene derivative together with unreacted starting material. The NMR yield was calculated to be 71% based on analysis of crude ^{1}H NMR spectrum. After the first column chromatography to get rid of the unreacted starting materials, the mixture of product and styrene derivative was subjected to HPLC separation that gave rise to 25 mg pure product (54% yield) as pale yellow oil. HPLC condtions: compound was dissolved in a 1 ml volume of DMSO. The separation was executed on an XBridge 19x100 mm 5 μm columns at a flow rate of 44 ml/min. Aqueous mobile phase A consisted of 0.1% formic acid in water, and organic mobile phase B was 0.1% formic acid in acetonitrile. Purification fractions were immediately frozen at -50°C and lyophilized for 24hrs using the Genesis Virtis. After lyophilization the compound was transferred to a preweighed vial using dichloromethane. IR (neat, cm^{-1}) 3067, 2954, 2860, 1703, 1602,

1490, 1452, 1429, 1383, 1302, 1250, 1165, 1131, 1050, 1023, 992; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1 H), 7.53-7.51 (m, 2 H), 7.44-7.40 (m, 1 H), 7.36-7.33 (m, 3 H), 6.97 (dd, *J* = 7.5, 7.5 Hz, 1 H), 6.92 (d, *J* = 7.5 Hz, 1 H), 5.91 (t, *J* = 8.0 Hz, 1 H), 4.38 (t, *J* = 5.2 Hz, 2 H), 4.06 (t, *J* = 5.0 Hz, 2 H), 2.42-2.37 (m, 2 H), 2.18-2.15 (m, 2 H), 1.89-1.84 (m, 2 H), 1.73-1.68 (m, 2 H), 1.59-1.52 (m, 2 H), 0.35 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.5, 157.7, 141.7, 139.4, 138.8, 134.0, 133.1, 132.2, 128.8, 127.7, 121.1, 120.0, 112.1, 67.5, 63.8, 30.1, 28.4, 28.2, 25.9, 25.7, -3.1; HRMS (ESI-TOF) calcd. for $C_{24}H_{30}O_3Si$ $[M+Na]^+$ 417.18564, found 417.18593.

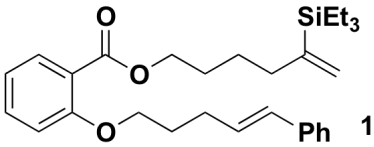


5-(Triethylsilyl)hex-5-en-1-yl 2-(pent-4-en-1-yloxy)benzoate (12f')

Yield 38% (colorless oil); IR (neat, cm^{-1}) 3077, 3048, 2951, 2911, 2875, 1729, 1704, 1641, 1601, 1582, 1491, 1453, 1416, 1385, 1301, 1250, 1164, 1133, 1078, 1050, 1013; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1 H), 7.44-7.41 (m, 1 H), 6.97-6.94 (m, 2 H), 5.85 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1 H), 5.65-5.64 (m, 1 H), 5.32-5.31 (m, 1 H), 5.08-5.04 (m, 1 H), 4.99 (d, *J* = 10.0 Hz, 1 H), 4.30 (t, *J* = 6.5 Hz, 2 H), 4.04 (t, *J* = 6.5 Hz, 2 H), 2.27 (dt, *J* = 7.2, 7.2 Hz, 2 H), 2.14 (t, *J* = 7.8 Hz, 2 H), 1.93 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.76 (tt, *J* = 7.1, 7.1 Hz, 2 H), 1.60-1.54 (m, 2 H), 0.92 (t, *J* = 8.0 Hz, 6 H), 0.60 (q, *J* = 8.0 Hz, 9 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.4, 148.5, 137.7, 133.1, 131.5, 125.3, 120.8, 120.0, 115.2, 113.1, 68.0, 64.8, 35.7, 30.0, 28.6, 28.3, 25.1, 7.3, 2.9; HRMS (ESI-TOF) calcd. for $C_{24}H_{38}O_3Si$ $[M+H]^+$ 403.26630, found 403.26630.

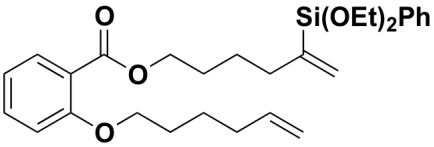


12f and



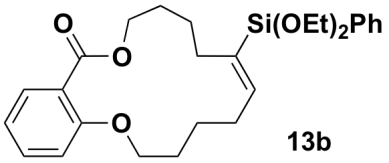
12f'-s

RCM reaction of compound **12f'** gave rise to an inseparable mixture of product **12f** and styrene derivative. Unreacted starting material and acyclic dimer were also observed. The NMR yield was calculated to be 10% based on analysis of crude ^{1}H NMR spectrum.

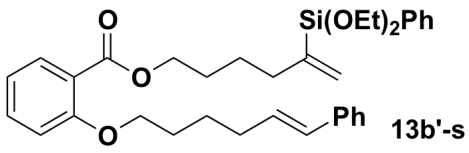


5-(Diethoxy(phenyl)silyl)hex-5-en-1-yl 2-(hex-5-en-1-yloxy)benzoate (13b')

Yield 76% (colorless oil); IR (neat, cm^{-1}) 3071, 2973, 2938, 1729, 1704, 1640, 1601, 1583, 1491, 1470, 1453, 1430, 1389, 1301, 1250, 1164, 1119, 1102, 1079, 997, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1 H), 7.64-7.62 (m, 2 H), 7.44-7.33 (m, 4 H), 6.96-6.93 (m, 2 H), 5.85-5.77 (m, 2 H), 5.67-5.66 (m, 1 H), 5.04-5.00 (m, 1 H), 4.96 (d, *J* = 10.0 Hz, 1 H), 4.22 (t, *J* = 7.0 Hz, 2 H), 4.02 (t, *J* = 6.2 Hz, 2 H), 3.81 (q, *J* = 7.0 Hz, 4 H), 2.22 (t, *J* = 7.8 Hz, 2 H), 2.11 (dt, *J* = 5.5, 5.5 Hz, 2 H), 1.83 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.70 (tt, *J* = 7.2, 7.2 Hz, 2 H), 1.62-1.52 (m, 4 H), 1.23 (t, *J* = 7.2 Hz, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.5, 145.5, 138.5, 134.6, 133.3, 133.1, 131.5, 130.0, 129.4, 127.7, 120.9, 119.9, 114.7, 113.0, 68.6, 64.8, 58.7, 35.2, 33.4, 28.6, 28.4, 25.2, 25.1, 18.3; HRMS (ESI-TOF) calcd. for $C_{29}H_{40}O_5Si$ $[M+Na]^+$ 519.25372, found 519.25541.

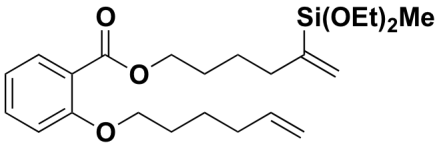


13b and



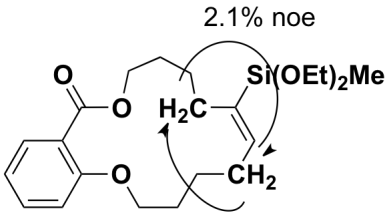
13b'-s

RCM reaction of compound **13b'** gave rise to an inseparable mixture of product **13b** and styrene derivative **13b'-s** as well as acyclic dimers and unreacted starting material. The NMR yield was calculated to be 35% based on analysis of crude ^{1}H NMR spectrum.



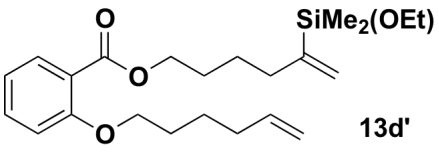
5-(Diethoxy(methyl)silyl)hex-5-en-1-yl 2-(hex-5-en-1-yloxy)benzoate (13c')

Yield 79% (colorless oil); IR (neat, cm^{-1}) 3076, 2972, 2940, 1729, 1705, 1641, 1601, 1491, 1452, 1389, 1301, 1252, 1164, 1103, 1079, 996, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1 H), 7.44-7.40 (m, 1 H), 6.96-6.93 (m, 2 H), 5.82 (ddt, *J* = 17.0, 10.5 , 6.5 Hz, 1 H), 5.69-5.69 (m, 1 H), 5.57-5.56 (m, 1 H), 5.05-5.01 (m, 1 H), 4.97 (d, *J* = 10.5 Hz, 1 H), 4.30 (t, *J* = 6.8 Hz, 2 H), 4.03 (t, *J* = 6.5 Hz, 2 H), 3.76 (q, *J* = 7.0 Hz, 4 H), 2.21 (t, *J* = 7.5 Hz, 2 H), 2.13 (dt, *J* = 7.2, 7.2 Hz, 2 H), 1.84 (tt, *J* = 7.1, 7.1 Hz, 2 H), 1.76 (tt, *J* = 7.2, 7.2 Hz, 2 H), 1.63-1.57 (m, 4 H), 1.21 (t, *J* = 7.0 Hz, 6 H), 0.19 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.5, 147.1, 138.5, 133.1, 131.5, 127.6, 120.8, 119.9, 114.7, 113.0, 68.6, 64.8, 58.2, 35.1, 33.4, 28.6, 28.5, 25.2, 25.1, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{24}H_{38}O_5Si$ $[M+Na]^+$ 457.23807, found 457.24010.

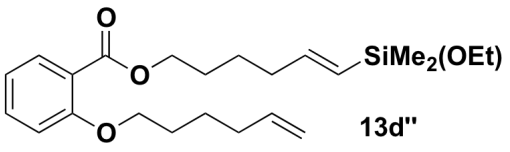


(*E*)-7-(Diethoxy(methyl)silyl)-4,5,8,9,10,11-hexahydro-2*H*-benzo[*b*][1,5]dioxacyclopentadecin-13(3*H*)-one (13c)

Yield 76% (pale yellow oil); IR (neat, cm^{-1}) 2969, 2928, 1700, 1602, 1491, 1452, 1387, 1302, 1251, 1165, 1130, 1103, 1078, 1016, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.76-7.74 (m, 1 H), 7.42-7.39 (m, 1 H), 6.96 (dd, *J* = 7.5, 7.5 Hz, 1 H), 6.92 (d, *J* = 7.5 Hz, 1 H), 6.13 (t, *J* = 7.5 Hz, 1 H), 4.40 (t, *J* = 5.5 Hz, 2 H), 4.08 (t, *J* = 5.0 Hz, 2 H), 3.74 (q, *J* = 6.8 Hz, 4 H), 2.25-2.21 (m, 4 H), 1.87-1.76 (m, 4 H), 1.68-1.56 (m, 4 H), 1.21 (t, *J* = 6.8 Hz, 6 H), 0.17 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.2, 157.7, 143.5, 137.5, 132.9, 131.7, 121.2, 120.0, 112.3, 68.3, 64.6, 58.1, 28.9, 28.8, 28.6, 28.0, 26.9, 26.7, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{22}H_{34}O_5Si$ $[M+Na]^+$ 429.20677, found 429.20692.

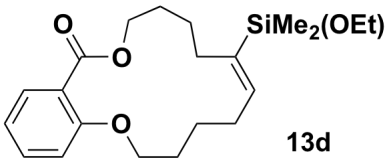


13d' and

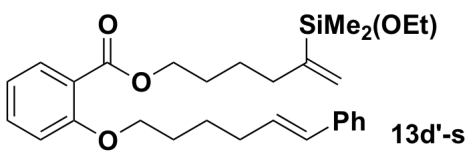


13d''

Hydrosilylation reaction gave rise to a 14.3:1 mixture of two regioisomers with the desired regio isomer **19d'** being the major one. Yield 89% (colorless oil).

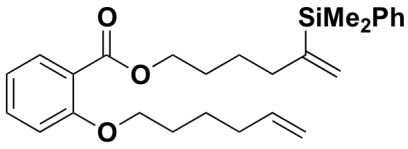


13d and



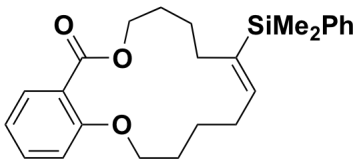
13d'-s

RCM reaction of the mixture **13d'** and **13d''** gave rise to an inseparable mixture of product **13d** and styrene derivative as well as acyclic dimer and unreacted starting material. The NMR yield was calculated to be 62% based on analysis of crude ^{1}H NMR spectrum.



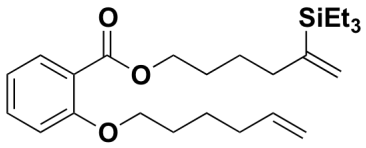
5-(Dimethyl(phenyl)silyl)hex-5-en-1-yl 2-(hex-5-en-1-yloxy)benzoate (13e')

Yield 74% (colorless oil); IR (neat, cm^{-1}) 3069, 2945, 1728, 1703, 1641, 1601, 1491, 1452, 1430, 1388, 1301, 1250, 1164, 1133, 1077, 1049, 996; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1 H), 7.51-7.49 (m, 2 H), 7.44-7.40 (m, 1 H), 7.34-7.31 (m, 3 H), 6.96-6.93 (m, 2 H), 5.81 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1 H), 5.70-5.69 (m, 1 H), 5.43-5.42 (m, 1 H), 5.04-5.00 (m, 1 H), 4.96 (d, *J* = 9.5 Hz, 1 H), 4.21 (t, *J* = 6.5 Hz, 2 H), 4.02 (t, *J* = 6.2 Hz, 2 H), 2.17 (t, *J* = 7.8 Hz, 2 H), 2.11 (dt, *J* = 7.2, 7.2 Hz, 2 H), 1.83 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.67 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.58 (tt, *J* = 7.5, 7.5 Hz, 2 H), 1.52-1.46 (m, 2 H), 0.37 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.6, 158.5, 149.9, 138.5, 138.2, 133.8, 133.1, 131.5, 128.9, 127.7, 126.0, 120.8, 119.9, 114.7, 113.0, 68.6, 64.7, 35.4, 33.4, 28.6, 28.4, 25.2, 25.1, -3.0; HRMS (ESI-TOF) calcd. for $C_{27}H_{36}O_3Si$ $[M+H]^+$ 437.25065, found 437.25057.



(*E*)-7-(dimethyl(phenyl)silyl)-4,5,8,9,10,11-hexahydro-2*H*-benzo[*b*][1,5]dioxacyclopentadecin-13(3*H*)-one (13e)

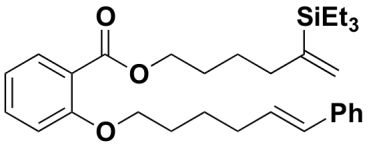
Yield 32% (pale yellow oil); IR (neat, cm^{-1}) 3067, 2952, 2859, 1698, 1601, 1490, 1452, 1429, 1383, 1302, 1249, 1165, 1132, 1108, 1049, 1015, 963; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.77-7.75 (m, 1 H), 7.51-7.49 (m, 2 H), 7.43-7.39 (m, 1 H), 7.34-7.33 (m, 3 H), 6.95 (dd, *J* = 7.8, 7.8 Hz, 1 H), 6.92 (d, *J* = 9.0 Hz, 1 H), 5.94 (t, *J* = 7.2 Hz, 1 H), 4.34 (t, *J* = 5.5 Hz, 2 H), 4.08 (t, *J* = 5.2 Hz, 2 H), 2.25-2.18 (m, 4 H), 1.87-1.82 (m, 2 H), 1.70-1.61 (m, 4 H), 1.46 (tt, *J* = 7.9 Hz, 2 H), 0.34 (s, 6 H); ^{13}C-NMR (125 MHz, C_6D_6) δ 168.2, 157.7, 142.2, 139.8, 139.0, 134.0, 133.0, 131.8, 128.8, 127.6, 121.1, 120.0, 112.3, 68.3, 64.6, 29.0, 28.9, 28.9, 28.8, 27.0, 27.0, -2.6; HRMS (ESI-TOF) calcd. for $C_{25}H_{32}O_3Si$ $[M+Na]^+$ 431.20129, found 431.20247.



5-(Triethylsilyl)hex-5-en-1-yl 2-(hex-5-en-1-yloxy)benzoate (13f')

Yield 56% (colorless oil); IR (neat, cm^{-1}) 3076, 3047, 2951, 2911, 2874, 1730, 1704, 1641, 1601, 1583, 1491, 1453, 1416, 1385, 1301, 1249, 1164, 1132, 1077, 1049, 1017, 959; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1 H), 7.44-7.41 (m, 1 H), 6.97-6.94 (m, 2 H), 5.82 (ddt, *J* = 17.0, 10.0, 6.8 Hz, 1 H), 5.65-5.64 (m, 1 H), 5.32-5.31 (m, 1 H), 5.05-5.01 (m, 1 H), 4.98-4.96 (m, 1 H), 4.30 (t, *J* = 6.8 Hz, 2 H), 4.03 (t, *J* = 6.8 Hz, 2 H), 2.16-2.11 (m, 4 H), 1.85 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.76 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.63-1.54 (m, 4 H), 0.92 (t, *J* = 8.0 Hz, 6 H), 0.60 (q, *J* = 8.0 Hz, 9 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.7, 158.5, 148.6, 138.5, 133.1, 131.5, 125.3, 120.8, 120.0, 114.7, 113.1,

68.6, 64.8, 35.7, 33.4, 28.6, 28.6, 25.2, 25.1, 7.3, 2.9; HRMS (ESI-TOF) calcd. for $C_{25}H_{40}O_3Si$ $[M+Na]^+$ 439.26389, found 439.26459.



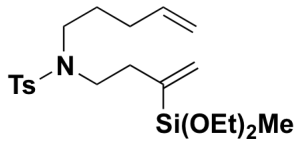
13f'-s

RCM reaction of compound **13f'** gave rise to less than 2% product based on analysis of crude ^{1}H NMR spectrum. Styrene derivative **13f'-s**, unreacted starting material and acyclic dimer were observed.

E. RCM of various vinylsiloxane substrates and protodesilylation of the alkenyl siloxane products

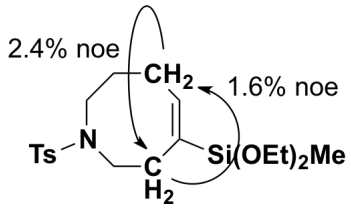
The RCM reactions were performed under optimized reaction conditions (see before).

Protodesilylation: adapted from the literature procedure,[165] the alkenyl siloxane product (1 equiv.) from the RCM reaction was dissolved in a anhydrous THF to a final concentration of 0.25 M. AgF (0.5 equiv.) was added to the solution immediately followed by acetic acid (1.5 equiv.) and TBAF (2.5 equiv., 1 M solution in THF). The reaction was kept in dark and stirred for 2 hours. The resulting mixture was filtered with celite, concentrated *in vacuo* and the residue was purified by silica gel column chromatography using Hexanes/EtOAc as eluent.



***N*-(3-(Diethoxy(methyl)silyl)but-3-enyl)-4-methyl-*N*-(pent-4-enyl)benzenesulfonamide (4c')**

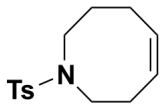
Yield 70% (colorless oil); IR (neat, cm^{-1}) 3051, 2974, 2926, 2878, 1641, 1599, 1494, 1444, 1390, 1342, 1306, 1258, 1159, 1103, 1079, 955; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 5.77 (ddt, *J* = 17.2, 10.2, 6.5 Hz, 1 H), 5.70 (d, *J* = 1.2 Hz, 1 H), 5.58 (d, *J* = 1.2 Hz, 1 H), 5.01 (d, *J* = 17.2 Hz, 1 H), 4.97 (d, *J* = 10.2 Hz, 1 H), 3.74 (q, *J* = 7.0 Hz, 4 H), 3.22-3.19 (m, 2 H), 3.14 (t, *J* = 7.8 Hz, 2 H), 2.41 (s, 3 H), 2.35 (t, *J* = 8.0 Hz, 2 H), 2.06 (dt, *J* = 7.0, 7.0 Hz, 2 H), 1.69-1.63 (m, 2 H), 1.20 (t, *J* = 7.0 Hz, 6 H), 0.18 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.1, 142.9, 137.5, 137.2, 130.0, 129.5, 127.1, 115.2, 58.3, 48.0, 47.8, 35.1, 30.8, 27.7, 21.4, 18.3, -4.9; HRMS (ESI-TOF) calcd. for $C_{21}H_{35}NO_4SSi$ $[M+Na]^+$ 448.19483, found 448.19573.



(*E*)-6-(Diethoxy(methyl)silyl)-1-tosyl-1,2,3,4,7,8-hexahydroazocine (4c)

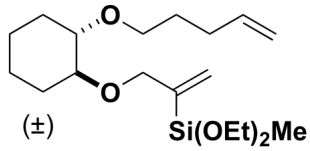
Yield 75% (pale yellow oil); IR (neat, cm^{-1}) 2972, 2926, 1615, 1455, 1389, 1338, 1292, 1257, 1158, 1079, 1050, 1017, 995; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 6.28 (t, *J* = 8.2 Hz, 1 H), 3.72 (q, *J* = 7.2 Hz, 4 H), 3.15 (bs, 2 H), 3.02 (t, *J* = 5.5 Hz, 2 H), 2.44 (t, *J* = 5.0 Hz, 2 H), 2.41 (s, 3 H), 2.32 (dt, *J* = 6.8, 6.8 Hz, 2 H), 1.79-1.74 (m, 2 H), 1.19 (t, *J* = 7.0 Hz, 6 H), 0.15 (s, 3 H); ^{13}C-NMR (125

MHz, $CDCl_3$) δ 143.8, 142.8, 137.0, 137.0, 129.6, 126.8, 58.2, 50.8, 48.2, 29.2, 29.1, 24.8, 21.4, 18.3, -4.9; HRMS (ESI-TOF) calcd. for $C_{19}H_{31}NO_4SSi$ $[M+H]^+$ 398.18159, found 398.27160.



(*Z*)-1-tosyl-1,2,3,4,7,8-hexahydroazocine (33-*Z*)

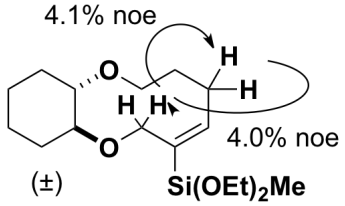
Yield 72% (colorless oil); IR (neat, cm^{-1}) 3018, 2933, 2858, 1598, 1494, 1456, 1369, 1333, 1304, 1289, 1157, 1112, 1091, 1060, 1038, 991; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2 H), 7.27 (d, *J* = 8.5 Hz, 2 H), 5.74-5.66 (m, 2 H), 3.14 (t, *J* = 5.0 Hz, 2 H), 3.08 (t, *J* = 5.5 Hz, 2 H), 2.40 (s, 3 H), 2.31-2.28 (m, 2 H), 2.22 (dt, *J* = 6.9, 6.9 Hz, 2 H), 1.76-1.72 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.9, 136.9, 131.3, 129.5, 128.2, 126.8, 50.8, 48.2, 29.4, 28.1, 23.3, 21.4; HRMS (ESI-TOF) calcd. for $C_{14}H_{19}NO_2S$ $[M+H]^+$ 266.12093, found 266.12097.



Diethoxy(methyl)(3-((1*S*,2*S*)-2-(pent-4-enyloxy)cyclohexyloxy)prop-1-en-2-yl)silane and its enantiomer (15')

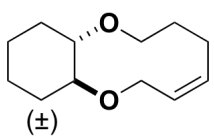
Yield 62% (colorless oil); IR (neat, cm^{-1}) 3077, 2974, 2934, 2865, 1641, 1449, 1390, 1366, 1295, 1257, 1164, 1104, 1083, 992, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.00-5.98 (m, 1 H), 5.82 (dddd, *J* = 17.0, 10.0, 6.5, 6.5 Hz, 1 H), 5.64-5.63 (m, 1 H), 5.03-4.99 (m, 1 H), 4.96-4.93 (m, 1 H), 4.24-4.23 (m, 2 H), 3.77 (q, *J* = 7.0 Hz, 4 H), 3.59-3.50 (m, 2

H), 3.26-3.18 (m, 2 H), 2.14-2.10 (m, 2 H), 1.97-1.94 (m, 2 H), 1.68-1.62 (m, 4 H), 1.35-1.19 (m, 10 H), 0.22 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.8, 138.5, 126.9, 114.5, 81.1, 80.6, 72.4, 69.1, 58.3, 30.4, 29.8, 29.8, 29.5, 23.3, 23.3, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{19}H_{36}O_4Si$ $[M+Na]^+$ 379.22751, found 379.22440.



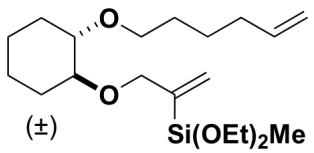
((8a*S*,12a*S*,*E*)-2,5,6,7,8a,9,10,11,12,12a-Decahydrobenzo[*b*][1,4]dioxecin-3-yl)diethoxy(methyl)silane and its enantiomer (15)

Yield 87% (pale yellow oil); IR (neat, cm^{-1}) 2972, 2932, 2862, 1615, 1451, 1390, 1364, 1256, 1165, 1113, 1082, 1009, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.22 (dd, *J* = 10.2, 6.8 Hz, 1 H), 4.33 (d, *J* = 10.5 Hz, 1 H), 4.26 (d, *J* = 10.5 Hz, 1 H), 3.81-3.76 (m, 4 H), 3.72-3.68 (m, 1 H), 3.62-3.57 (m, 1 H), 3.22-3.17 (m, 1 H), 3.02-2.97 (m, 1 H), 2.68-2.60 (m, 1 H), 2.18-2.12 (m, 1 H), 2.00-1.98 (m, 1 H), 1.94-1.92 (m, 1 H), 1.90-1.82 (m, 1 H), 1.66-1.65 (m, 2 H), 1.54-1.48 (m, 1 H), 1.26-1.12 (m, 10 H), 0.21 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 146.8, 136.6, 83.2, 83.1, 67.6, 66.7, 58.3, 31.8, 31.8, 28.6, 25.1, 24.7, 24.5, 18.3, -4.4; HRMS (ESI-TOF) calcd. for $C_{17}H_{32}O_4Si$ $[M+Na]^+$ 351.19621, found 351.19793.



(8a*S*,12a*S*,*Z*)-2,3,4,7,8a,9,10,11,12,12a-decahydrobenzo[*b*][1,4]dioxecine and its enantiomer (34-*Z*)

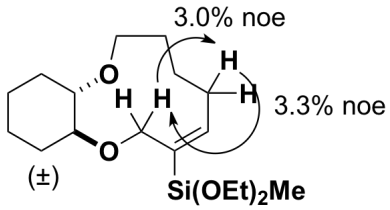
Yield 86% (colorless oil); IR (neat, cm^{-1}) 3012, 2930, 2858, 1451, 1360, 1315, 1239, 1206, 1117, 1086, 1051, 1026, 970; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.79 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1 H), 5.55 (ddd, *J* = 10.7, 10.7, 6.5 Hz, 1 H), 4.31 (dd, *J* = 10.5, 10.5 Hz, 1 H), 4.19 (dd, *J* = 10.7, 5.2 Hz, 1 H), 3.70-3.67 (m, 1 H), 3.53-3.49 (m, 1 H), 3.20-3.15 (m, 1 H), 2.96-2.92 (m, 1 H), 2.65-2.59 (m, 1 H), 1.94-1.80 (m, 4 H), 1.64-1.63 (m, 2 H), 1.43-1.37 (m, 1 H), 1.22-1.10 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 131.7, 128.8, 84.7, 83.2, 67.3, 66.9, 32.2, 31.6, 28.1, 24.6, 24.5, 22.6; HRMS (ESI-TOF) calcd. for $C_{12}H_{20}O_2$ $[M+H]^+$ 197.15361, found 197.15343.



Diethoxy(3-((1*S*,2*S*)-2-(hex-5-enyloxy)cyclohexyloxy)prop-1-en-2-yl)(methyl)silane and its enantiomer (16')

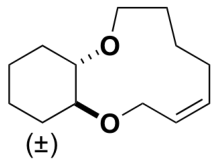
Yield 64% (colorless oil); IR (neat, cm^{-1}) 3076, 2974, 2934, 2863, 1641, 1451, 1390, 1366, 1295, 1257, 1164, 1104, 1083, 993, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.99-5.98 (m, 1 H), 5.80 (dddd, *J* = 17.0, 10.5, 7.0, 7.0 Hz, 1 H), 5.64-5.62 (m, 1 H), 5.01-4.98 (m, 1 H), 4.94-4.92 (m, 1 H), 4.23-4.23 (m, 2 H), 3.77 (q, *J* = 7.0 Hz, 4 H), 3.58-3.49 (m, 2 H), 3.25-3.18 (m, 2 H), 2.08-2.04 (m, 2 H), 1.97-1.93 (m, 2 H), 1.65-1.62 (m, 2 H), 1.60-1.54 (m, 2 H), 1.48-1.42 (m, 2 H), 1.35-1.19 (m, 10 H), 0.22 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.8, 138.8, 126.9, 114.4, 81.1, 80.6, 72.4, 69.6, 58.3, 33.6, 29.8, 29.8,

25.6, 23.3, 23.3, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{20}H_{38}O_4Si$ $[M+Na]^+$ 393.24316, found 393.24372.



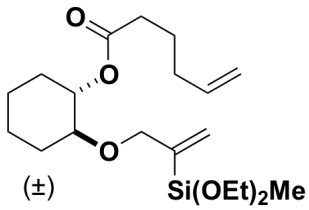
((9a*S*,13a*S*,*E*)-5,6,7,8,9a,10,11,12,13,13a-Decahydro-2*H*-benzo[*b*][1,4]dioxacycloundecin-3-yl)diethoxy(methyl)silane and its enantiomer (16)

Yield 36% (pale yellow oil); IR (neat, cm^{-1}) 2971, 2929, 2860, 1618, 1450, 1389, 1371, 1255, 1191, 1165, 1104, 1079, 1044, 1003, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.23 (dd, *J* = 10.0, 6.0 Hz, 1 H), 4.24 (d, *J* = 10.2 Hz, 1 H), 4.14 (d, *J* = 10.2 Hz, 1 H), 3.85-3.82 (m, 1 H), 3.77 (q, *J* = 7.0 Hz, 4 H), 3.54-3.51 (m, 1 H), 3.14-3.09 (m, 1 H), 3.00-2.97 (m, 1 H), 2.66-2.58 (m, 1 H), 2.24-2.18 (m, 1 H), 2.10-2.08 (m, 1 H), 2.00-1.98 (m, 1 H), 1.75-1.66 (m, 4 H), 1.59-1.52 (m, 1 H), 1.44-1.39 (m, 1 H), 1.23-1.08 (m, 10 H), 0.19 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 149.7, 133.4, 84.1, 82.2, 71.9, 66.2, 58.2, 31.5, 31.1, 28.4, 27.2, 27.0, 24.5, 24.3, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{18}H_{34}O_4Si$ $[M+Na]^+$ 365.21186, found 365.21302.



(9a*S*,13a*S*,*Z*)-3,4,5,8,9a,10,11,12,13,13a-decahydro-2*H*-benzo[*b*][1,4]dioxacycloundecine and its enantiomer (35-*Z*)

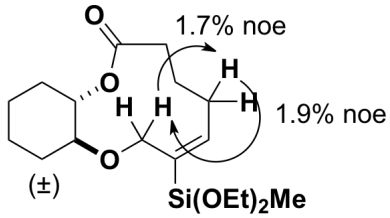
Yield 90% (colorless oil); IR (neat, cm^{-1}) 3012, 2930, 2858, 1450, 1370, 1312, 1243, 1188, 1130, 1102, 999; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.65 (ddd, *J* = 9.5, 9.5, 5.0 Hz, 1 H), 5.56 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1 H), 4.28 (dd, *J* = 10.0, 10.0 Hz, 1 H), 4.06 (dd, *J* = 10.0, 5.0 Hz, 1 H), 3.70 (dd, *J* = 10.0, 8.0 Hz, 1 H), 3.47 (dd, *J* = 11.5, 6.5 Hz, 1 H), 3.14 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1 H), 2.98 (ddd, *J* = 9.5, 9.5, 5.0 Hz, 1 H), 2.63-2.56 (m, 1 H), 2.04-2.00 (m, 3 H), 1.73-1.64 (m, 4 H), 1.51-1.45 (m, 1 H), 1.42-1.37 (m, 1 H), 1.19-1.07 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.0, 126.1, 84.3, 82.1, 71.0, 66.4, 31.9, 30.7, 28.2, 26.7, 26.1, 24.5, 24.2; HRMS (ESI-TOF) calcd. for $C_{13}H_{22}O_2$ $[M+H]^+$ 211.16926, found 211.16944.



(1*S*,2*S*)-2-((2-(Diethoxy(methyl)silyl)allyl)oxy)cyclohexyl hex-5-enoate and its enantiomer (17')

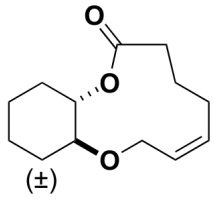
Yield 65% (colorless oil); IR (neat, cm^{-1}) 3077, 2973, 2938, 2866, 1736, 1641, 1452, 1389, 1365, 1254, 1168, 1103, 1080, 1009, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.93-5.93 (m, 1 H), 5.78 (dddd, *J* = 17.0, 10.5, 6.5, 6.5 Hz, 1 H), 5.62-5.62 (m, 1 H), 5.04-5.00 (m, 1 H), 4.98 (d, *J* = 10.0 Hz, 1 H), 4.81 (ddd, *J* = 8.5, 8.5, 4.5 Hz, 1 H), 4.20 (d, *J* = 13.0 Hz, 1 H), 4.10 (d, *J* = 13.0 Hz, 1 H), 3.76 (q, *J* = 7.0 Hz, 4 H), 3.32 (ddd, *J* = 8.5, 8.5, 4.0 Hz, 1 H), 2.31 (dd, *J* = 8.0, 8.0 Hz, 2 H), 2.09 (ddd, *J* = 7.0, 7.0, 7.0 Hz, 2 H), 2.03-1.97 (m, 2 H), 1.76-1.64 (m, 4 H), 1.44-1.33 (m, 3 H), 1.30-1.20 (m, 7 H), 0.20 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.9, 144.4, 137.8, 127.1, 115.2, 78.7, 74.7, 72.0, 58.3, 58.3,

33.9, 33.0, 29.6, 29.5, 24.1, 23.1, 23.0, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{20}H_{36}O_5Si$ $[M+Na]^+$ 407.22242, found 407.22435.



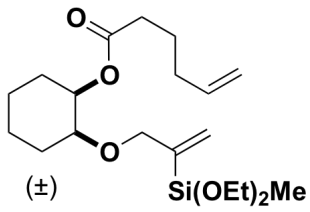
(9a*S*,13a*S*,*E*)-7-(Diethoxy(methyl)silyl)-3,4,5,8,9a,10,11,12,13,13a-decahydro-2*H*-benzo[*b*][1,4]dioxacycloundecin-2-one and its enantiomer (17)

Yield 43% (pale yellow oil); IR (neat, cm^{-1}) 2971, 2932, 2865, 1736, 1614, 1450, 1389, 1365, 1256, 1225, 1196, 1152, 1084, 1055, 983, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.20-6.17 (m, 1 H), 4.75 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1 H), 4.22 (d, *J* = 12.8 Hz, 1 H), 3.99 (d, *J* = 12.8 Hz, 1 H), 3.81-3.73 (m, 4H), 3.21 (ddd, *J* = 10.0, 10.0, 4.5 Hz, 1 H), 2.85-2.76 (m, 1 H), 2.37-2.26 (m, 2 H), 2.16-2.12 (m, 2 H), 2.06-1.99 (m, 1 H), 1.95-1.93 (m, 1 H), 1.83-1.70 (m, 3 H), 1.34-1.16 (m, 10 H), 0.20 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.4, 150.2, 135.5, 79.4, 75.0, 63.3, 58.2, 58.2, 33.3, 30.6, 30.1, 27.1, 24.1, 23.6, 18.4, 18.3, -4.9; HRMS (ESI-TOF) calcd. for $C_{18}H_{32}O_5Si$ $[M+H]^+$ 357.20918, found 357.20950.



(9a*S*,13a*S*,*Z*)-3,4,5,8,9a,10,11,12,13,13a-decahydro-2*H*-benzo[*b*][1,4]dioxacycloundecin-2-one and its enantiomer (36-*Z*)

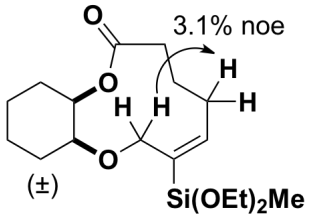
Yield 83% (colorless oil); IR (neat, cm^{-1}) 3011, 2936, 2862, 1735, 1451, 1364, 1322, 1217, 1153, 1087, 1032, 984; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.63-6.59 (m, 1 H), 5.54 (ddd, *J* = 10.5, 8.0, 8.0 Hz, 1 H), 4.73-4.68 (m, 1 H), 4.20 (dd, *J* = 13.2, 4.8 Hz, 1 H), 3.94 (dd, *J* = 13.2, 7.2 Hz, 1 H), 3.24-3.19 (m, 1 H), 2.50-2.43 (m, 1 H), 2.36-2.26 (m, 2 H), 2.16-2.03 (m, 2 H), 1.97-1.85 (m, 2 H), 1.82-1.67 (m, 3 H), 1.33-1.13 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.2, 134.6, 127.3, 80.1, 75.8, 64.3, 33.9, 30.9, 30.5, 25.9, 24.0, 23.9, 23.8; HRMS (ESI-TOF) calcd. for $C_{13}H_{20}O_3$ $[M+Na]^+$ 247.13047, found 247.13070.



(1*R*,2*S*)-2-((2-(Diethoxy(methyl)silyl)allyl)oxy)cyclohexyl hex-5-enoate and its enantiomer (18')

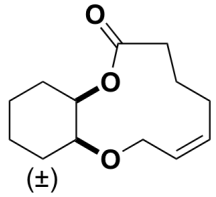
Yield 69% (colorless oil); IR (neat, cm^{-1}) 3077, 2973, 2939, 2869, 1733, 1641, 1449, 1388, 1364, 1255, 1170, 1104, 1082, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.94-5.93 (m, 1 H), 5.78 (dddd, *J* = 16.8, 10.2, 6.8, 6.8 Hz, 1 H), 5.64-5.63 (m, 1 H), 5.08-5.07 (m, 1 H), 5.04-5.00 (m, 1 H), 4.98 (d, *J* = 10.0 Hz, 1 H), 4.14 (d, *J* = 13.0 Hz, 1 H), 4.10 (d, *J* = 13.0 Hz, 1 H), 3.79-3.75 (m, 4 H), 3.49-3.48 (m, 1 H), 2.34 (dd, *J* = 7.5, 7.5 Hz, 2 H), 2.09 (ddd, *J* = 7.0, 7.0, 7.0 Hz, 2 H), 1.93-1.88 (m, 1 H), 1.85-1.78 (m, 1 H), 1.76-1.65 (m, 3 H), 1.62-1.47 (m, 3 H), 1.43-1.29 (m, 2 H), 1.23-1.20 (m, 6 H), 0.22 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.1, 144.4, 137.8, 127.4, 115.2, 76.5, 71.6, 58.3, 33.9, 33.0,

27.8, 27.8, 24.2, 22.0, 21.8, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{20}H_{36}O_5Si$ $[M+Na]^+$ 407.22242, found 407.22426.



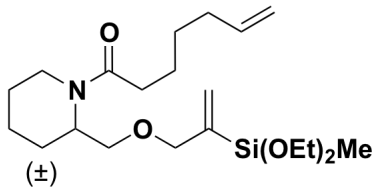
(9a*S*,13a*R*,*E*)-7-(Diethoxy(methyl)silyl)-3,4,5,8,9a,10,11,12,13,13a-decahydro-2*H*-benzo[*b*][1,4]dioxacycloundecin-2-one and its enantiomer (18)

Yield 36% (pale yellow oil); IR (neat, cm^{-1}) 2970, 2931, 2870, 1730, 1614, 1450, 1390, 1360, 1246, 1225, 1162, 1110, 1080, 1049, 949; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.24 (dd, *J* = 9.8, 6.2 Hz, 1 H), 4.67 (ddd, *J* = 11.0, 3.8, 3.8 Hz, 1 H), 4.29 (d, *J* = 11.5 Hz, 1 H), 3.89 (bs, 1 H), 3.86 (d, *J* = 11.5 Hz, 1 H), 3.80-3.75 (m, 4 H), 2.45 (ddd, *J* = 13.2, 8.2, 4.8 Hz, 1 H), 2.25-2.13 (m, 3 H), 1.94-1.88 (m, 2 H), 1.86-1.78 (m, 2 H), 1.72-1.70 (m, 1 H), 1.59-1.48 (m, 2 H), 1.42-1.17 (m, 9 H), 0.21 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.6, 147.9, 134.7, 75.6, 74.0, 65.8, 58.3, 34.7, 28.6, 27.6, 26.5, 24.9, 23.7, 19.9, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{18}H_{32}O_5Si$ $[M+H]^+$ 357.20918, found 357.21015.



(9a*S*,13a*R*,*Z*)-3,4,5,8,9a,10,11,12,13,13a-decahydro-2*H*-benzo[*b*][1,4]dioxacycloundecin-2-one and its enantiomer (37-*Z*)

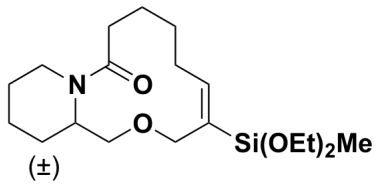
Yield 92% (colorless oil), inseparable mixture with styrene derivative; IR (neat, cm^{-1}) 3010, 2937, 2862, 1729, 1448, 1359, 1243, 1212, 1155, 1083, 1051, 1014; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.61-5.52 (m, 2 H), 4.66-4.62 (m, 1 H), 4.50 (dd, *J* = 12.2, 7.8 Hz, 1 H), 4.05 (bs, 1 H), 3.93 (dd, *J* = 12.2, 5.0 Hz, 1 H), 2.33-2.29 (m, 2 H), 2.24-2.10 (m, 2 H), 1.93-1.79 (m, 4 H), 1.74-1.72 (m, 1 H), 1.59-1.50 (m, 2 H), 1.47-1.27 (m 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.5, 133.7, 127.6, 75.5, 72.3, 64.8, 35.0, 30.1, 26.3, 26.1, 24.9, 24.1, 19.7; HRMS (ESI-TOF) calcd. for $C_{13}H_{20}O_3$ $[M+Na]^+$ 247.13047, found 247.13029.



(±)-1-(2-(((2-(Diethoxy(methyl)silyl)allyl)oxy)methyl)piperidin-1-yl)hept-6-en-1-one (19')

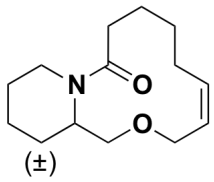
Yield 54% (pale yellow oil); IR (neat, cm^{-1}) 3075, 2973, 2930, 2865, 1644, 1425, 1390, 1365, 1257, 1166, 1103, 1081, 1029, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.89 and 5.87 (pair of bs due to rotamers, 1 H), 5.80 (dddd, *J* = 17.0, 10.0, 6.8, 6.8 Hz, 1 H), 5.64 (bs, 1 H), 5.01-4.98 (m, 1 H), 4.93 (d, *J* = 10.0 Hz, 1 H), 4.57 and 3.66 (pair of d due to rotamers, *J* = 13.0 Hz, 1 H), 4.14-4.04 (m, 3 H), 3.76 (q, *J* = 6.8 Hz, 4 H), 3.61-3.46 (m, 2 H), 3.11 and 2.57 (pair of dd due to rotamers, *J* = 13.0, 13.0 Hz, 1 H), 2.43-2.29 (m, 2 H), 2.07 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 2 H), 1.86-1.80 (m, 1 H), 1.71-1.49 (m, 6 H), 1.46-1.33 (m, 3 H), 1.21 (t, *J* = 7.0 Hz, 6 H), 0.20 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.4 and 171.8 (due to rotamers), 144.0 and 143.8 (due to rotamers), 138.7, 127.7,

114.4, 74.0 and 73.8 (due to rotamers), 68.7 and 68.4 (due to rotamers), 58.3, 52.4, 46.8, 42.2, 37.0, 33.6 and 33.2 (due to rotamers), 33.6, 28.7, 26.5 and 25.9 (due to rotamers), 25.2 and 25.1 (due to rotamers), 24.9 and 24.8 (due to rotamers), 19.6 and 19.4 (due to rotamers), 18.3, -4.5; HRMS (ESI-TOF) calcd. for $C_{21}H_{39}NO_4Si$ $[M+H]^+$ 398.27211, found 398.27371.



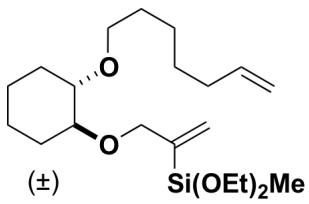
(±)-(*E*)-4-(Diethoxy(methyl)silyl)-1,6,7,8,9,12,13,14,15,15a-decahydropyrido[2,1-*c*][1,4]oxaazacyclododecin-10(3*H*)-one (19)

Yield 33% (colorless oil); IR (neat, cm^{-1}) 2970, 2928, 2865, 1634, 1444, 1389, 1366, 1256, 1165, 1106, 1079, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.15 (dd, *J* = 9.5, 5.5 Hz, 1 H), 4.65 (d, *J* = 13.0 Hz, 1 H), 4.40 (bs, 1 H), 4.29 (d, *J* = 11.2 Hz, 1 H), 3.95 (d, *J* = 11.2 Hz, 1 H), 3.79 (dd, *J* = 9.8, 9.8 Hz, 1 H), 3.73 (q, *J* = 6.9 Hz, 4 H), 3.33 (dd, *J* = 11.0, 4.5 Hz, 1 H), 2.85-2.82 (m, 1 H), 2.59-2.55 (m, 2 H), 1.96-1.92 (m, 2 H), 1.74-1.58 (m, 6 H), 1.48-1.35 (m, 4 H), 1.19 (dd, *J* = 6.8, 6.8 Hz, 6 H), 0.16 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.7, 148.0, 132.9, 67.6, 67.4, 58.3 52.0, 36.6, 29.3, 27.3, 27.0, 26.9, 25.3, 23.8, 19.7, 18.3, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{19}H_{35}NO_4Si$ $[M+Na]^+$ 392.22276, found 392.22352.



(±)-(*Z*)-1,6,7,8,9,12,13,14,15,15a-decahydropyrido[2,1-*c*][1,4]oxaazacyclododecin-10(3*H*)-one (38-*Z*)

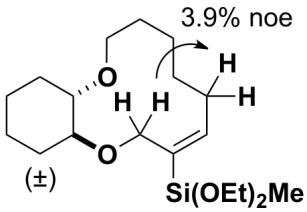
Yield 90% (colorless oil); IR (neat, cm^{-1}) 3010, 2934, 2861, 1631, 1444, 1419, 1367, 1327, 1266, 1125, 1078, 1029; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.59-5.49 (m, 2 H), 4.61-4.59 (m, 1 H), 4.36 (bs, 1 H), 4.24-4.20 (m, 1 H), 3.84-3.82 (m, 1 H), 3.76 (dd, *J* = 9.8, 9.8 Hz, 1 H), 3.43-3.40 (m, 1 H), 2.74 (bs, 1 H), 2.53 (dd, *J* = 12.2, 12.2 Hz, 1 H), 2.38 (bs, 1 H), 1.93-1.92 (m, 2 H), 1.73-1.60 (m, 6 H), 1.44-1.30 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.3, 134.9, 125.4, 67.3, 65.5, 51.1, 36.8, 29.5, 26.8, 26.4, 25.2, 25.1, 23.6, 19.4; HRMS (ESI-TOF) calcd. for $C_{14}H_{23}NO_2$ $[M+Na]^+$ 260.16210, found 260.16176.



Diethoxy(3-(((1S,2S)-2-(hept-6-en-1-yloxy)cyclohexyl)oxy)prop-1-en-2-yl)(methyl)silane and its enantiomer (20')

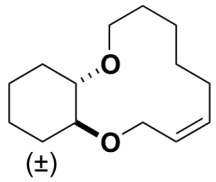
Yield 59% (colorless oil); IR (neat, cm^{-1}) 3076, 2974, 2933, 2862, 1641, 1451, 1390, 1366, 1295, 1257, 1164, 1104, 1083, 994, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.99-5.98 (m, 1 H), 5.80 (dddd, *J* = 17.0, 10.5, 6.8, 6.8 Hz, 1 H), 5.64-5.63 (m, 1 H), 5.01-4.97 (m, 1 H), 4.94-4.92 (m, 1 H), 4.23-4.23 (m, 2 H), 3.77 (q, *J* = 7.0 Hz, 4 H), 3.57-3.48 (m, 2

H), 3.25-3.18 (m, 2 H), 2.04 (ddd, J = 7.0, 7.0, 7.0 Hz, 2 H), 1.96-1.94 (m, 2 H), 1.65-1.62 (m, 2 H), 1.59-1.53 (m, 2 H), 1.41-1.19 (m, 14 H), 0.22 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.8, 139.0, 126.9, 114.2, 81.1, 80.7, 72.4, 69.8, 58.3, 33.7, 30.2, 29.8, 29.8, 28.8, 25.7, 23.3, 23.3, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{21}H_{40}O_4Si$ $[M+Na]^+$ 407.25881, found 407.25995.



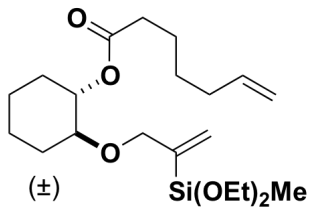
((10a*S*,14a*S*,*E*)-2,5,6,7,8,9,10a,11,12,13,14,14a-Dodecahydrobenzo[*b*][1,4]dioxacyclododecin-3-yl)diethoxy(methyl)silane and its enantiomer (20)

Yield 59% (pale yellow oil); IR (neat, cm^{-1}) 2970, 2930, 2859, 1616, 1450, 1389, 1365, 1254, 1166, 1135, 1111, 1083, 1024, 950; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.33 (dd, J = 8.8, 6.8 Hz, 1 H), 4.35 (d, J = 8.8 Hz, 1 H), 4.07 (d, J = 8.8 Hz, 1 H), 3.92-3.89 (m, 1 H), 3.79-3.74 (m, 4 H), 3.16-3.12 (m, 1 H), 3.09-3.05 (m, 2 H), 2.62-2.55 (m, 1 H), 2.08-2.03 (m, 2 H), 2.00-1.94 (m, 1 H), 1.68-1.59 (m, 4 H), 1.56-1.46 (m, 4 H), 1.22-1.08 (m, 10 H), 0.19 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 149.7, 133.7, 84.2, 81.4, 70.0, 66.5, 58.2, 58.2, 31.2, 30.7, 27.7, 27.4, 27.2, 25.8, 24.5, 24.2, 18.3, -4.5; HRMS (ESI-TOF) calcd. for $C_{19}H_{36}O_4Si$ $[M+Na]^+$ 379.22751, found 379.22910.



(10a*S*,14a*S*,*Z*)-2,3,4,5,6,9,10a,11,12,13,14,14a-dodecahydrobenzo[*b*][1,4]dioxacyclododecine and its enantiomer (39-*Z*)

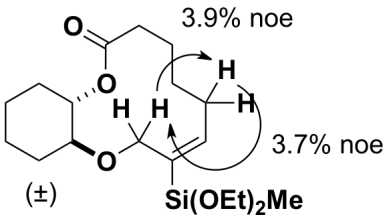
Yield 88% (colorless oil), inseparable mixture with styrene derivative; IR (neat, cm^{-1}) 3014, 2930, 2858, 1451, 1361, 1334, 1313, 1244, 1190, 1130, 1107, 1047, 983, 962; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.73-5.65 (m, 2 H), 4.47 (dd, *J* = 9.0, 9.0 Hz, 1 H), 3.96 (dd, *J* = 9.2, 4.2 Hz, 1 H), 3.93-3.90 (m, 1 H), 3.16-3.08 (m, 3 H), 2.45-2.38 (m, 1 H), 2.08-2.07 (m, 1 H), 2.00-1.98 (m, 1 H), 1.90-1.86 (m, 1 H), 1.70-1.60 (m, 3 H), 1.52-1.45 (m, 4 H), 1.28-1.13 (m, 5 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 135.4, 126.3, 84.8, 80.8, 69.6, 66.0, 31.5, 30.6, 28.1, 27.3, 24.9, 24.6, 24.1, 24.0; HRMS (ESI-TOF) calcd. for $C_{14}H_{24}O_2$ $[M+Na]^+$ 247.16685, found 247.16800.



(1*S*,2*S*)-2-((2-(Diethoxy(methyl)silyl)allyl)oxy)cyclohexyl hept-6-enoate and its enantiomer (21')

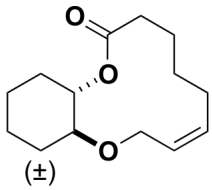
Yield 60% (colorless oil); IR (neat, cm^{-1}) 3075, 2973, 2937, 2865, 1736, 1641, 1452, 1389, 1257, 1166, 1103, 1080, 1008, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.93-5.93 (m, 1 H), 5.79 (dddd, *J* = 17.0, 10.5, 6.5, 6.5 Hz, 1 H), 5.62-5.62 (m, 1 H), 5.02-4.98 (m, 1 H), 4.95 (d, *J* = 10.0 Hz, 1 H), 4.81 (ddd, *J* = 8.2, 8.2, 4.5 Hz, 1 H), 4.21 (d, *J* = 13.2 Hz, 1

H), 4.10 (d, *J* = 13.2 Hz, 1 H), 3.76 (q, *J* = 7.0 Hz, 4 H), 3.32 (ddd, *J* = 8.5, 8.5, 4.0 Hz, 1 H), 2.30 (dd, *J* = 8.0, 8.0 Hz, 2 H), 2.08-1.96 (m, 4 H), 1.71-1.61 (m, 4 H), 1.45-1.39 (m, 3 H), 1.34 (dd, *J* = 9.5, 9.5 Hz, 2 H), 1.30-1.20 (m, 7 H), 0.21 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.0, 144.4, 138.4, 127.1, 114.6, 78.7, 74.6, 72.0, 58.3, 58.3, 34.5, 33.4, 29.6, 29.5, 28.3, 24.4, 23.1, 23.0, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{21}H_{38}O_5Si$ $[M+Na]^+$ 421.23807, found 421.23885.



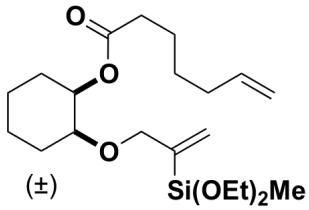
(10a*S*,14a*S*,*E*)-8-(Diethoxy(methyl)silyl)-3,4,5,6,10a,11,12,13,14,14a-decahydrobenzo[*b*][1,4]dioxacyclododecin-2(9*H*)-one and its enantiomer (21)

Yield 82% (pale yellow oil); IR (neat, cm^{-1}) 2971, 2936, 2866, 1734, 1617, 1451, 1389, 1360, 1338, 1256, 1225, 1189, 1150, 1104, 1082, 1036, 996, 950; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.37 (dd, *J* = 10.2, 5.8 Hz, 1 H), 4.61 (ddd, *J* = 10.2, 10.2, 4.5 Hz, 1 H), 4.10 (d, *J* = 9.0 Hz, 1 H), 4.04 (d, *J* = 9.0 Hz, 1 H), 3.76-3.71 (m, 4 H), 3.22 (ddd, *J* = 10.0, 10.0, 4.5 Hz, 1 H), 2.66 (dddd, *J* = 11.3, 11.3, 11.3, 4.0 Hz, 1 H), 2.47 (ddd, *J* = 12.5, 12.5, 4.5 Hz, 1 H), 2.35 (ddd, *J* = 13.2, 4.8, 4.8 Hz, 1 H), 2.16-2.15 (m, 1 H), 2.07-2.06 (m, 1 H), 1.96-1.90 (m, 1 H), 1.85-1.78 (m, 1 H), 1.74-1.69 (m, 2 H), 1.65-1.56 (m, 2 H), 1.33-1.18 (m, 11 H), 0.17 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.8, 151.1, 132.6, 80.4, 76.5, 65.4, 58.3, 58.2, 33.3, 31.0, 30.2, 27.9, 27.7, 24.9, 24.1, 24.0, 18.3, -4.9; HRMS (ESI-TOF) calcd. for $C_{19}H_{34}O_5Si$ $[M+H]^+$ 371.22483, found 371.22556.



(10a*S*,14a*S*,*Z*)-3,4,5,6,10a,11,12,13,14,14a-decahydrobenzo[*b*][1,4]dioxacyclododecin-2(9*H*)-one and its enantiomer (40-*Z*)

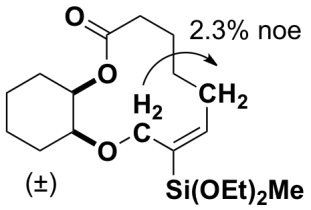
Yield 91% (colorless oil); IR (neat, cm^{-1}) 3019, 2937, 2862, 1732, 1451, 1354, 1278, 1222, 1150, 1107, 1085, 1034, 989; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 10.0, 10.0, 5.5 Hz, 1 H), 5.65 (ddd, *J* = 10.0, 7.0, 7.0 Hz, 1 H), 4.62 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1 H), 4.06 (dd, *J* = 8.5, 8.5 Hz, 1 H), 3.98 (dd, *J* = 9.5, 6.5 Hz, 1 H), 3.22 (ddd, *J* = 10.0, 10.0, 4.0 Hz, 1 H), 2.55 (dddd, *J* = 11.5, 11.5, 11.5, 4.0 Hz, 1 H), 2.46 (ddd, *J* = 12.5, 12.5, 4.0 Hz, 1 H), 2.35 (ddd, *J* = 13.0, 5.0, 5.0 Hz, 1 H), 2.11-2.06 (m, 2 H), 1.94-1.87 (m, 1 H), 1.76-1.67 (m, 3 H), 1.65-1.55 (m, 2 H), 1.34-1.17 (m, 5 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.6, 138.1, 124.6, 80.6, 76.7, 65.2, 33.1, 30.9, 30.6, 28.2, 25.9, 24.6, 24.2, 23.9; HRMS (ESI-TOF) calcd. for $C_{14}H_{22}O_3$ $[M+Na]^+$ 261.14612, found 261.14610.



(1*R*,2*S*)-2-((2-(Diethoxy(methyl)silyl)allyl)oxy)cyclohexyl hept-6-enoate and its enantiomer (22')

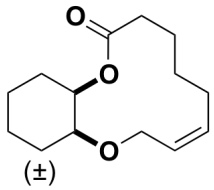
Yield 66% (colorless oil); IR (neat, cm^{-1}) 3076, 2972, 2938, 2866, 1734, 1641, 1449, 1388, 1364, 1257, 1169, 1104, 1081, 992, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.94-5.93

(m, 1 H), 5.79 (dddd, *J* = 17.0, 10.5, 6.5, 6.5 Hz, 1 H), 5.64-5.63 (m, 1 H), 5.08-5.06 (m, 1 H), 5.02-4.98 (m, 1 H), 4.94 (d, *J* = 10.0 Hz, 1 H), 4.14 (d, *J* = 13.0 Hz, 1 H), 4.10 (d, *J* = 13.0 Hz, 1 H), 3.79-3.75 (m, 4 H), 3.49-3.48 (m, 1 H), 2.33 (dd, *J* = 7.2, 7.2 Hz, 2 H), 2.06 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 2 H), 1.93-1.87 (m, 1 H), 1.85-1.78 (m, 1 H), 1.70-1.47 (m, 6 H), 1.46-1.29 (m, 4 H), 1.21 (dd, *J* = 7.0, 7.0 Hz, 6 H), 0.22 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.2, 144.4, 138.5, 127.4, 114.6, 76.5, 71.6, 58.3, 34.5, 33.4, 28.3, 27.8, 27.8, 24.5, 22.0, 21.9, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{21}H_{38}O_5Si$ $[M+Na]^+$ 421.23807, found 421.23931.



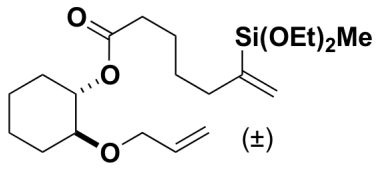
(10a*S*,14a*R*,*E*)-8-(Diethoxy(methyl)silyl)-3,4,5,6,10a,11,12,13,14,14a-decahydrobenzo[*b*][1,4]dioxacyclododecin-2(9*H*)-one and its enantiomer (22)

Yield 46% (pale yellow oil); IR (neat, cm^{-1}) 2970, 2935, 2864, 1730, 1616, 1449, 1389, 1353, 1256, 1224, 1156, 1105, 1079, 984, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.26 (dd, *J* = 8.2, 6.8 Hz, 1 H), 5.02-5.00 (m, 1 H), 4.06-4.01 (m, 2 H), 3.78-3.73 (m, 4 H), 3.61-3.60 (m, 1 H), 2.40-2.28 (m, 2 H), 2.27-2.15 (m, 2 H), 1.96-1.90 (m, 1 H), 1.88-1.78 (m, 2 H), 1.75-1.68 (m, 1 H), 1.67-1.54 (m, 6 H), 1.40-1.29 (m, 2 H), 1.22-1.19 (m, 6 H), 0.18 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.3, 149.6, 133.3, 75.0, 71.9, 63.6, 58.3, 58.2, 34.9, 29.7, 28.6, 27.9, 27.7, 27.6, 24.4, 22.1, 21.7, 18.3, -4.8; HRMS (ESI-TOF) calcd. for $C_{19}H_{34}O_5Si$ $[M+Na]^+$ 393.20677, found 393.20690.



(10a*S*,14a*R*,*Z*)-3,4,5,6,10a,11,12,13,14,14a-decahydrobenzo[*b*][1,4]dioxacyclododecin-2(9*H*)-one and its enantiomer (41-*Z*)

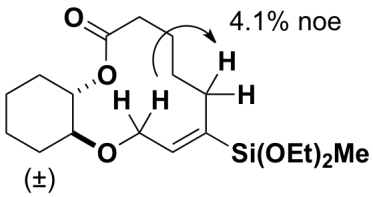
Yield 97% (colorless oil); IR (neat, cm^{-1}) 2935, 2859, 1729, 1449, 1352, 1219, 1147, 1081, 1047; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.71 (ddd, *J* = 10.5, 8.0, 8.0 Hz, 1 H), 5.61 (ddd, *J* = 10.5, 6.5, 6.5 Hz, 1 H), 5.07-5.06 (m, 1 H), 4.09-4.00 (m, 2 H), 3.65-3.63 (m, 1 H), 2.43-2.38 (m, 1 H), 2.34-2.29 (m, 1 H), 2.26-2.18 (m, 1 H), 2.10-2.03 (m, 1 H), 1.99-1.94 (m, 1 H), 1.83-1.72 (m, 3 H), 1.71-1.50 (m, 6 H), 1.42-1.28 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.3, 136.3, 125.4, 74.3, 71.9, 62.8, 34.6, 28.7, 28.3, 27.5, 26.1, 23.9, 22.2, 21.6; HRMS (ESI-TOF) calcd. for $C_{14}H_{22}O_3$ $[M+Na]^+$ 261.14612, found 261.14045.



(1*S*,2*S*)-2-(Allyloxy)cyclohexyl 6-(diethoxy(methyl)silyl)hept-6-enoate and its enantiomer (23')

Yield 82% (colorless oil); IR (neat, cm^{-1}) 3075, 2973, 2937, 2865, 1736, 1641, 1452, 1389, 1364, 1257, 1166, 1102, 1080, 1008, 994, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.91-5.84 (m, 1 H), 5.67 (bs, 1 H), 5.55-5.55 (m, 1 H), 5.25 (d, *J* = 17.5 Hz, 1 H), 5.13 (d, *J* = 10.0 Hz, 1 H), 4.80-4.76 (m, 1 H), 4.09 (dd, *J* = 12.8, 5.2 Hz, 1 H), 4.01 (dd, *J* = 12.8,

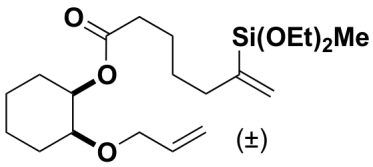
5.2 Hz, 1 H), 3.76 (q, *J* = 7.0 Hz, 4 H), 3.32-3.28 (m, 1 H), 2.31 (dd, *J* = 7.8, 7.8 Hz, 2 H), 2.16 (dd, *J* = 7.8, 7.8 Hz, 2 H), 2.00-1.97 (m, 2 H), 1.71-1.62 (m, 4 H), 1.52-1.46 (m, 2 H), 1.41-1.20 (m, 10 H), 0.19 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.0, 147.1, 135.4, 127.5, 116.2, 78.4, 74.7, 70.4, 58.2, 35.1, 34.6, 29.9, 29.7, 28.2, 24.9, 23.2, 23.2, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{21}H_{38}O_5Si$ $[M+Na]^+$ 421.23807, found 421.24013.



(10a*S*,14a*S*,*E*)-7-(Diethoxy(methyl)silyl)-3,4,5,6,10a,11,12,13,14,14a-decahydrobenzo[*b*][1,4]dioxacyclododecin-2(9*H*)-one and its enantiomer (23)

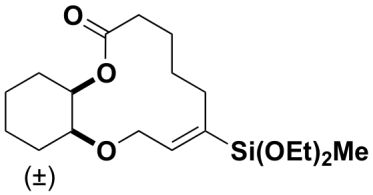
Yield 79% (pale yellow oil); IR (neat, cm^{-1}) 2971, 2937, 2866, 1733, 1450, 1390, 1353, 1339, 1256, 1227, 1146, 1103, 1081, 1036, 996, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.21 (dd, *J* = 7.0, 7.0 Hz, 1H), 4.65-4.60 (m, 1 H), 4.20 (dd, *J* = 8.5, 8.5 Hz, 1 H), 3.98 (dd, *J* = 9.0, 6.0 Hz, 1 H), 3.76-3.72 (m, 4 H), 3.23 (ddd, *J* = 10.0, 10.0, 4.0 Hz, 1 H), 2.58 (ddd, *J* = 12.5, 12.5, 3.5 Hz, 1 H), 2.54-2.48 (m, 1 H), 2.34 (ddd, *J* = 13.0, 5.0, 5.0 Hz, 1 H), 2.10 (bs, 2 H), 1.95-1.87 (m, 2 H), 1.76-1.69 (m, 3 H), 1.64-1.57 (m, 1 H), 1.33-1.18 (m, 11 H), 0.18 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.7, 146.5, 136.5, 80.7, 77.1, 65.8, 58.2, 58.2, 33.4, 31.0, 30.7, 29.0, 27.8, 25.5, 24.3, 23.9, 18.3, 18.3, -4.7; HRMS (ESI-TOF) calcd. for $C_{19}H_{34}O_5Si$ $[M+H]^+$ 371.22483, found 371.22591.

Protodesilylation of **23** generated **40-*Z*** with 52% yield.



(1*R*,2*S*)-2-(Allyloxy)cyclohexyl 6-(diethoxy(methyl)silyl)hept-6-enoate and its enantiomer (24')

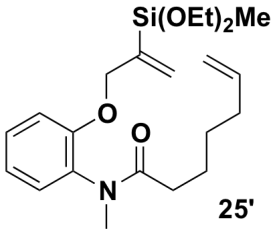
Yield 80% (colorless oil); IR (neat, cm^{-1}) 3051, 2971, 2938, 2866, 1733, 1449, 1388, 1365, 1257, 1238, 1168, 1104, 1081, 950; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.92-5.84 (m, 1 H), 5.68-5.67 (m, 1 H), 5.55-5.54 (m, 1 H), 5.28-5.24 (m, 1 H), 5.15-5.12 (m, 1 H), 5.09-5.08 (m, 1H), 4.05 (dd, *J* = 13.0, 5.8 Hz, 1H), 3.98 (dd, *J* = 13.2, 5.8 Hz, 1 H), 3.76 (q, *J* = 7.0 Hz, 4 H), 3.49-3.47 (m, 1 H), 2.35 (dd, *J* = 7.5, 7.5 Hz, 2 H), 2.16 (dd, *J* = 7.5, 7.5 Hz, 2 H), 1.91-1.86 (m, 1 H), 1.83-1.76 (m, 1 H), 1.71-1.62 (m, 3 H), 1.60-1.46 (m, 5 H), 1.43-1.29 (m, 2 H), 1.21 (dd, *J* = 7.0, 7.0 Hz, 6 H), 0.18 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.3, 174.1, 135.3, 127.5, 116.5, 76.0, 71.0, 69.7, 58.2, 35.1, 34.6, 28.2, 27.9, 27.8, 24.9, 22.1, 21.7, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{21}H_{38}O_5Si$ $[M+Na]^+$ 421.23807, found 421.23908.



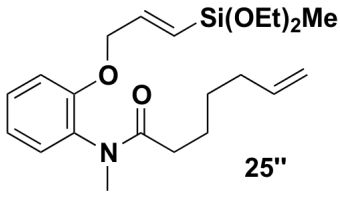
(10a*S*,14a*R*,*E*)-7-(Diethoxy(methyl)silyl)-3,4,5,6,10a,11,12,13,14,14a-decahydrobenzo[*b*][1,4]dioxacyclododecin-2(9*H*)-one and its enantiomer (24)

Yield 14% (colorless oil); IR (neat, cm^{-1}) 2970, 2935, 2865, 1731, 1449, 1390, 1354, 1256, 1226, 1149, 1103, 1079, 986, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.14 (dd, *J* = 6.5, 6.5 Hz, 1 H), 5.06-5.05 (m, 1H), 4.19 (dd, *J* = 10.8, 6.5 Hz, 1 H), 4.03 (dd, *J* = 10.8, 6.5 Hz, 1 H), 3.77-3.72 (m, 4 H), 3.60-3.59 (m, 1 H), 2.46-2.40 (m, 2 H), 2.34 (ddd, *J* = 13.0, 5.5, 5.5 Hz, 1 H), 2.08 (ddd, *J* = 12.2, 12.2, 5.0 Hz, 1 H), 1.98-1.92 (m, 1 H), 1.84-1.71 (m, 3 H), 1.68-1.54 (m, 5 H), 1.50-1.28 (m, 3 H), 1.20 (dd, *J* = 7.5, 7.5 Hz, 6 H), 0.18 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.0, 144.2, 137.3, 74.8, 72.3, 63.9, 58.2, 34.0, 29.7, 28.3, 28.1, 28.0, 27.4, 25.1, 22.3, 21.4, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{19}H_{34}O_5Si$ $[M+H]^+$ 371.22483, found 371.22603.

Protodesilylation of **24** generated **41-*Z*** with 54% yield.

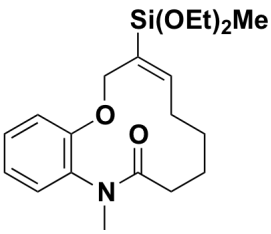


25' and



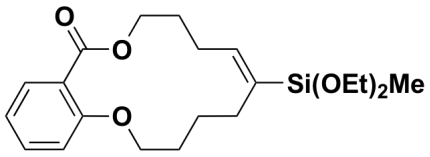
25''

Hydrosilylation reaction gave rise to a 6.1:1 mixture of two regioisomers with the desired regio isomer **25'** being the major one. Yield 75% (colorless oil).



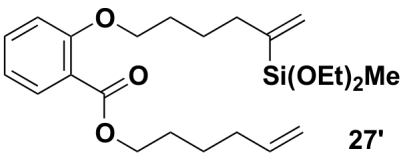
(*E*)-3-(diethoxy(methyl)silyl)-10-methyl-5,6,7,8-tetrahydro-2*H*-benzo[*b*][1,4]oxaazacy- clododecin-9(10*H*)-one (25)

Yield 64% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.34-7.30 (m, 1 H), 7.14-7.12 (m, 1H), 7.04-7.02 (m, 1 H), 6.99-6.95 (m, 1 H), 4.42-6.38 (m, 1 H), 3.80-3.75 (m, 4 H), 3.14 (s, 3 H), 2.32-2.26 (m, 1 H), 2.16-2.08 (m, 1 H), 2.00-1.92 (m, 1 H), 1.89-1.83 (m, 2 H), 1.70-1.62 (m, 1 H), 1.47-1.40 (m, 1 H), 1.33-1.25 (m, 1 H), 1.23-1.20 (m, 6 H), 0.22 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.6, 154.4, 153.1, 132.6, 130.0, 129.1, 128.9, 120.9, 112.5, 64.1, 58.4, 58.3, 36.5, 29.6, 27.5, 26.1, 23.7, 18.3, -5.0.

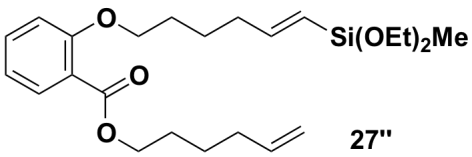


(*E*)-6-(diethoxy(methyl)silyl)-2,3,4,5,9,10-hexahydrobenzo[*b*][1,5]dioxacyclotetra-decin-12(8*H*)-one (26)

Yield 78% (colorless oil); IR (neat, cm^{-1}) 2970, 1704, 1601, 1489, 1453, 1300, 1252, 1164, 1101, 1078, 1020, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1 H), 7.43-7.40 (m, 1H), 7.01-6.96 (m, 2 H), 6.02 (t, J = 7.5 Hz, 1 H), 4.34 (t, J = 5.2 Hz, 2 H), 4.17 (t, J = 5.5 Hz, 2 H), 3.77-3.73 (m, 6 H), 2.40-2.35 (m, 2 H), 2.22-2.19 (m, 2 H), 1.86-1.77 (m, 4 H), 1.66-1.61 (m, 2 H), 1.22 (t, J = 6.7 Hz, 6 H), 1.22 (t, J = 6.7 Hz, 6 H), 0.18 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.2, 157.4, 143.0, 137.7, 132.9, 131.6, 121.9, 120.2, 113.1, 66.9 64.1, 58.1, 28.7, 28.4, 27.4, 26.0, 25.0, 18.3, -4.7; HRMS (ESI-TOF) calcd. for $C_{21}H_{32}O_5Si$ $[M+H]^+$ 393.20918, found 393.21212.

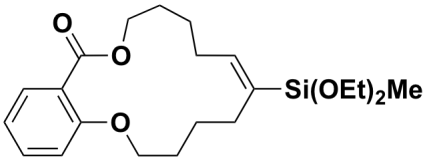


27' and



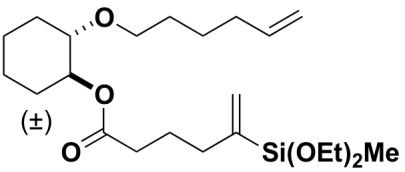
27''

Hydrosilylation reaction gave rise to a 14.3:1 mixture of two regioisomers with the desired regio isomer **27'** being the major one. Yield 82% (colorless oil).



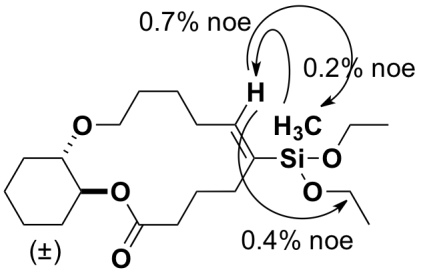
(*E*)-6-(diethoxy(methyl)silyl)-4,5,8,9,10,11-hexahydro-2*H*-benzo[*b*][1,5]dioxacyclo-pentadecin-13(3*H*)-one (27)

Yield 58% (colorless oil); IR (neat, cm^{-1}) 2969, 1700, 1602, 1492, 1453, 1388, 1302, 1253, 1165, 1130, 1078, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1 H), 7.42-7.38 (m, 1H), 6.95 (dd, *J* = 7.2, 7.2 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 6.11 (t, *J* = 7.5 Hz, 1 H), 4.41 (t, *J* = 5.7 Hz, 2 H), 4.02 (t, *J* = 5.2 Hz, 2 H), 3.76-3.72 (m, 4 H), 2.22-2.17 (m, 4 H), 1.85-1.78 (m, 4 H), 1.68-1.57 (m, 4 H), 1.21 (t, *J* = 6.2 Hz, 6 H), 0.17 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.4, 157.7, 144.0, 136.6, 132.9, 131.6, 121.0, 119.8, 112.0, 67.9, 64.3, 58.1, 29.4, 28.4, 28.1, 28.1 27.7, 26.0, 18.3, -4.8; HRMS (ESI-TOF) calcd. for $C_{22}H_{34}O_5Si$ $[M+H]^+$ 407.22483, found 407.22437.



(1*S*,2*S*)-2-(Hex-5-en-1-yloxy)cyclohexyl 5-(diethoxy(methyl)silyl)hex-5-enoate and its enantiomer (29')

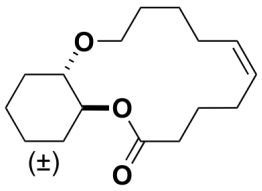
Yield 73% (colorless oil); IR (neat, cm^{-1}) 3076, 2972, 2938, 2866, 1735, 1641, 1452, 1389, 1256, 1165, 1109, 1082, 953; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.79 (dddd, *J* = 17.2, 10.2, 7.0, 7.0 Hz, 1 H), 5.69-5.69 (m, 1 H), 5.58-5.58 (m, 1 H), 5.01-4.97 (m, 1 H), 4.94 (d, *J* = 10.0 Hz, 1 H), 4.78-4.74 (m, 1 H), 3.76 (q, *J* = 7.0 Hz, 4 H), 3.56-3.52 (m, 1 H), 3.44-3.39 (m, 1 H), 3.24-3.19 (m, 1 H), 2.30 (dd, *J* = 7.5, 7.5 Hz, 2 H), 2.19 (dd, *J* = 7.5, 7.5 Hz, 2 H), 2.05 (ddd, *J* = 7.0, 7.0, 7.0 Hz, 2 H), 1.98-1.96 (m, 2 H), 1.82-1.76 (m, 2 H), 1.70-1.64 (m, 2 H), 1.56-1.50 (m, 2 H), 1.45-1.40 (m, 2 H), 1.36-1.31 (m, 3 H), 1.28-1.20 (m, 7 H), 0.20 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.9, 146.6, 138.8, 128.1, 114.4, 78.9, 74.6, 69.3, 58.2, 34.9, 34.2, 33.5, 29.8, 29.7, 29.6, 25.5, 24.1, 23.2, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{23}H_{42}O_5Si$ $[M+Na]^+$ 449.26937, found 449.27061.



(12a*S*,16a*S*,*E*)-6-(Diethoxy(methyl)silyl)-4,5,8,9,10,11,12a,13,14,15,16,16a-dodecahydrobenzo[*b*][1,4]dioxacyclotetradecin-2(3*H*)-one and its enantiomer (29)

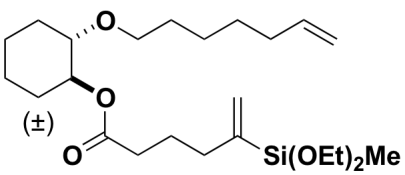
Yield 76% (pale yellow oil); IR (neat, cm^{-1}) 2930, 2865, 2733, 1731, 1612, 1452, 1389, 1367, 1338, 1293, 1252, 1212, 1191, 1165, 1110, 1080, 1020, 989, 951; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.08 (dd, *J* = 7.0, 7.0 Hz, 1H), 4.76 (ddd, *J* = 10.0, 10.0, 4.5 Hz, 1 H), 3.80-3.71 (m, 5 H), 3.28-3.22 (m, 2 H), 2.38-2.12 (m, 6 H), 2.07-1.99 (m, 2 H), 1.88-1.82

(m, 1 H), 1.74-1.52 (m, 6 H), 1.43-1.36 (m, 1 H), 1.32-1.18 (m, 10 H), 0.16 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.2, 145.5, 135.4, 79.8, 75.2, 67.7, 58.1, 33.4, 30.9, 29.6, 28.5, 28.3, 27.4, 27.1, 24.4, 24.1, 24.0, 18.3, -4.4; HRMS (ESI-TOF) calcd. for $C_{21}H_{38}O_5Si$ $[M+H]^+$ 399.25613, found 399.25752.



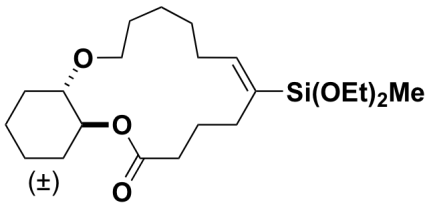
(12a*S*,16a*S*,*Z*)-4,5,8,9,10,11,12a,13,14,15,16,16a-dodecahydrobenzo[*b*][1,4]dioxacyclotetradecin-2(3*H*)-one and its enantiomer (43-*Z*)

Yield 60% (colorless oil), inseparable mixture with styrene; IR (neat, cm^{-1}) 3002, 2936, 2861, 1731, 1452, 1368, 1246, 1207, 1162, 1111, 1022; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.51 (ddd, *J* = 8.5, 8.5, 8.5 Hz, 1H), 5.24 (ddd, *J* = 10.0, 10.0, 6.5 Hz, 1H), 4.80 (ddd, *J* = 10.0, 10.0, 5.0 Hz, 1 H), 3.78-3.75 (m, 1 H), 3.25-3.20 (m, 2 H), 2.38-2.04 (m, 6 H), 1.99-1.83 (m, 3 H), 1.76-1.57 (m, 3 H), 1.55-1.37 (m, 4 H), 1.32-1.17 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.1, 131.6, 128.9, 79.8, 74.9, 66.9, 32.1, 30.9, 29.7, 28.3, 26.7, 26.6, 25.6, 24.1, 23.9, 23.7; HRMS (ESI-TOF) calcd. for $C_{16}H_{26}O_3$ $[M+Na]^+$ 289.17742, found 289.17804.



(1*S*,2*S*)-2-(Hept-6-en-1-yloxy)cyclohexyl 5-(diethoxy(methyl)silyl)hex-5-enoate and its enantiomer (30')

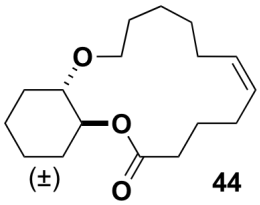
Yield 79% (colorless oil); IR (neat, cm^{-1}) 3077, 2973, 2937, 2865, 1736, 1641, 1452, 1389, 1256, 1166, 1110, 1082, 995, 953; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.80 (dddd, *J* = 17.0, 10.0, 6.8, 6.8 Hz, 1 H), 5.69-5.69 (m, 1 H), 5.58-5.58 (m, 1 H), 5.01-4.97 (m, 1 H), 4.93 (d, *J* = 10.0 Hz, 1 H), 4.76 (ddd, *J* = 8.5, 8.5, 4.5 Hz, 1 H), 3.76 (q, *J* = 7.0 Hz, 4 H), 3.53 (ddd, *J* = 9.0, 6.5, 6.5 Hz, 1 H), 3.41 (ddd, *J* = 9.5, 7.0, 7.0 Hz, 1 H), 3.21 (ddd, *J* = 8.5, 8.5, 4.0 Hz, 1 H), 2.30 (dd, *J* = 7.2, 7.2 Hz, 2 H), 2.19 (dd, *J* = 7.8, 7.8 Hz, 2 H), 2.04 (ddd, *J* = 7.2, 7.2, 7.2 Hz, 2 H), 1.98-1.96 (m, 2 H), 1.83-1.77 (m, 2 H), 1.70-1.64 (m, 2 H), 1.55-1.49 (m, 2 H), 1.42-1.20 (m, 14 H), 0.20 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.9, 146.6, 138.9, 128.1, 114.2, 78.9, 74.6, 69.5, 58.2, 34.9, 34.3, 33.7, 30.0, 29.8, 29.7, 28.7, 25.6, 24.1, 23.2, 18.3, -4.6; HRMS (ESI-TOF) calcd. for $C_{24}H_{44}O_5Si$ $[M+H]^+$ 441.30308, found 441.30151.



(13a*S*,17a*S*,*E*)-6-(Diethoxy(methyl)silyl)-3,4,5,8,9,10,11,12,13a,14,15,16,17,17a-tetradecahydro-2*H*-benzo[*b*][1,4]dioxacyclopentadecin-2-one and its enantiomer (30)

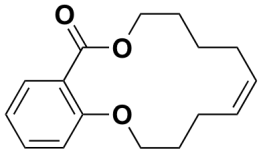
Yield 43% (pale yellow oil), *Z*:*E* = 8:92, *E* product was purified and characterized.; IR (neat, cm^{-1}) 2935, 2861, 1735, 1613, 1452, 1414, 1365, 1311, 1255, 1218, 1188, 1162, 1111, 1080, 1017, 988, 952; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.08 (dd, *J* = 10.5, 5.0 Hz, 1

H), 4.72 (ddd, J = 10.0, 10.0, 4.3 Hz, 1 H), 3.74 (q, J = 7.0Hz, 4 H), 3.68-3.65 (m, 1 H), 3.40-3.36 (m, 1 H), 3.15 (ddd, 9.5, 9.5, 4.5 Hz, 1 H), 2.55-2.49 (m, 1 H), 2.38-2.20 (m, 3 H), 2.12-2.07 (m, 2 H), 2.02-1.89 (m, 3 H), 1.72-1.62 (m, 4 H), 1.40-1.14 (m, 15 H), 0.17 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.3, 145.5, 135.3, 80.1, 76.4, 68.9, 58.1, 58.1, 32.4, 31.1, 31.0, 29.2, 28.8, 27.8, 27.3, 25.5, 24.2, 24.0, 23.5, 18.3, -4.3; HRMS (ESI-TOF) calcd. for $C_{22}H_{40}O_5Si$ $[M+H]^+$ 413.27178, found 413.27159.



44

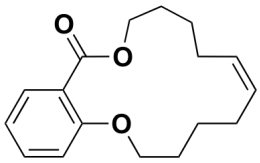
Protodesilylation of **30** (mixture of *Z* and *E* isomers with a ratio of 8:92) gave rise to **44** as an inseparable mixture of *Z* and *E* isomers with a ratio of 90:10 determined by ^{1}H NMR analysis.



(*Z*)-3,4,7,8,9,10-Hexahydrobenzo[*b*][1,5]dioxacyclotetradecin-12(2*H*)-one (14-*Z*)

Protodesilylation of 91 mg **12c** (0.22 mmol) followed by column chromatography (gradient 0 – 20% ethyl acetate/hexane) gave rise to 35 mg of the title compound. Yield 64% (colorless oil); IR (neat, cm^{-1}) 3009, 2935, 2865, 1703, 1601, 1581, 1490, 1453, 1384, 1354, 1302, 1250, 1165, 1132, 1097, 1049, 1015, 975; ^{1}H-NMR (500 MHz,

$CDCl_3$) δ 7.78-7.76 (m, 1 H), 7.44-7.40 (m, 1 H), 6.98-6.93 (m, 2 H), 5.68 (dt, *J* = 10.0, 8.2 Hz, 1 H), 5.48 (dt, *J* = 10.0, 8.2 Hz, 1 H), 4.43 (t, *J* = 6.0 Hz, 2 H), 4.09 (t, *J* = 5.2 Hz, 2 H), 2.29 (dt, *J* = 7.8, 7.8 Hz, 2 H), 2.13-2.08 (m, 2 H), 1.85-1.79 (m, 4 H), 1.69-1.63 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.5, 157.5, 133.1, 132.2, 130.1, 130.0, 121.3, 120.0, 112.2, 66.9, 63.8, 29.8, 27.6, 25.7, 25.4, 23.5; HRMS (ESI-TOF) calcd. for $C_{16}H_{20}O_3$ $[M+H]^+$ 261.14852, found 261.14455.



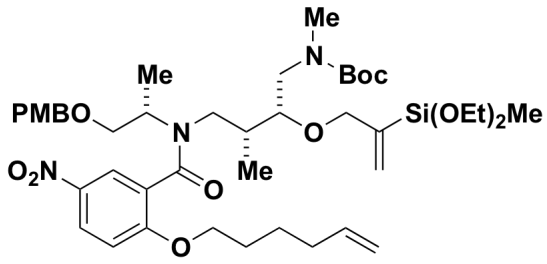
(*Z*)-4,5,8,9,10,11-Hexahydro-2*H*-benzo[*b*][1,5]dioxacyclopentadecin-13(3*H*)-one (42-*Z*)

Protodesilylation of **13c** (60 mg, 0.14 mmol) followed by column chromatography (gradient 0 – 20% ethyl acetate/hexane) gave rise to 17 mg of the title compound. Yield 46% (colorless oil); IR (neat, cm^{-1}) 3007, 2936, 2862, 1698, 1601, 1491, 1452, 1384, 1300, 1249, 1164, 1131, 1097, 1050, 958; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1 H), 7.42-7.38 (m, 1 H), 6.97-6.94 (m, 1 H), 6.91 (d, *J* = 8.0 Hz, 1 H), 5.55 (dt, *J* = 10.8, 7.4 Hz, 1 H), 5.50 (dt, *J* = 10.8, 7.4 Hz, 1 H), 4.40 (t, *J* = 6.0 Hz, 2 H), 4.04 (t, *J* = 5.2 Hz, 2 H), 2.14-2.09 (m, 4 H), 1.85-1.77 (m, 4 H), 1.65-1.59 (m, 2 H), 1.58-1.52 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.3, 157.6, 132.7, 131.2, 130.3, 129.8, 121.5, 120.0, 112.3, 68.3, 64.5, 28.6, 27.9, 27.1, 26.9, 26.4, 26.0; HRMS (ESI-TOF) calcd. for $C_{17}H_{22}O_3$ $[M+Na]^+$ 297.14612, found 297.14667.

F. Synthesis of compound 31 and 32 and determination of stereoselectivity

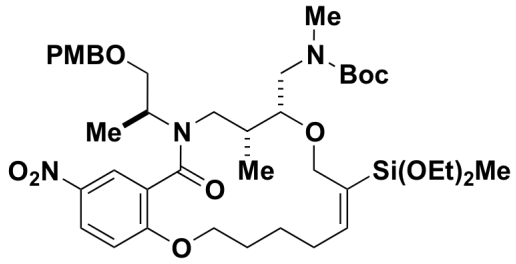
Following the reported procedure,[8] the alkyne substrates were synthesized. Hydrosilylation of the alkynes gave rise to the corresponding alkenyl siloxane **31'** and **32'**, which were subjected to the RCM reaction.

Note: The ^{1}H and ^{13}C NMR spectra of many of these compounds were extremely complicated owing to the various combinations of rotamers, and conformers. Efforts to completely coalesce the resonances through variable temperature NMR (up to 110 ^{o}C) were unsuccessful. Despite their complexity, all spectra are for single compounds that were larger than 95% pure by LC/MS.



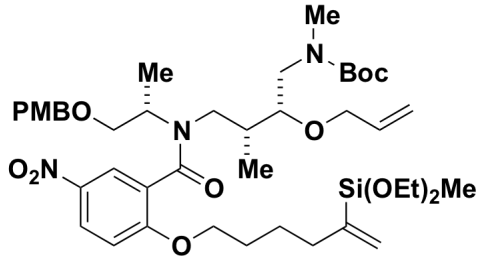
***tert*-Butyl (2*R*,3*R*)-2-(2-(diethoxy(methyl)silyl)allyloxy)-4-(2-(hex-5-enyloxy)-*N*-((*S*)-1-(4-methoxybenzyloxy)propan-2-yl)-5-nitrobenzamido)-3-methylbutyl(methyl)carbamate (31')**

Yield 69% (pale yellow oil); IR (neat, cm^{-1}) 2973, 2932, 1693, 1640, 1612, 1588, 1516, 1458, 1391, 1365, 1341, 1272, 1251, 1160, 1078, 1036, 952; HRMS (ESI-TOF) calcd. for $C_{43}H_{67}N_3O_{11}Si$ $[M+Na]^+$ 852.44371, found 852.44396; $[\alpha]_D^{21}$ = -25.5 (c = 2.2, $CHCl_3$).



***tert*-Butyl ((10*R*,11*R*,*E*)-7-(diethoxy(methyl)silyl)-13-((*S*)-1-(4-methoxybenzyloxy)propan-2-yl)-11-methyl-16-nitro-14-oxo-2,3,4,5,8,10,11,12,13,14-decahydrobenzo[*b*][1,9,5]dioxaazacyclohexadecin-10-yl)methyl(methyl)carbamate (31)**

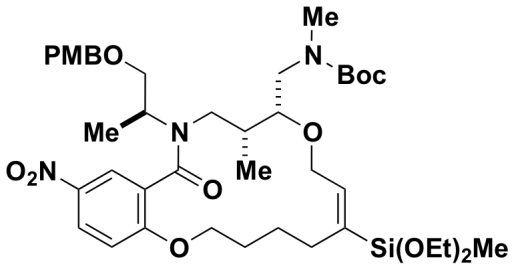
Z/*E* ratio is less than 1:99. Yield 47% (pale yellow oil); IR (neat, cm^{-1}) 2972, 2934, 1692, 1633, 1614, 1588, 1516, 1468, 1392, 1365, 1341, 1302, 1271, 1251, 1159, 1105, 1080, 1036, 1010, 986, 953; HRMS (ESI-TOF) calcd. for $C_{41}H_{63}N_3O_{11}Si$ $[M+Na]^+$ 824.41241, found 824.41263; $[\alpha]_D^{21}$ = -16.4 (c = 7.6, $CHCl_3$).



***tert*-Butyl ((2*R*,3*R*)-2-(allyloxy)-4-(2-((5-(diethoxy(methyl)silyl)hex-5-en-1-yl)oxy)-*N*-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-5-nitrobenzamido)-3-methylbutyl)(methyl)carbamate (32')**

Yield 69% (pale yellow oil); IR (neat, cm^{-1}) 2973, 2934, 1694, 1940, 1612, 1588, 1516, 1457, 1391, 1365, 1340, 1272, 1252, 1162, 1078, 1036, 952; HRMS (ESI-TOF) calcd.

for $C_{43}H_{67}N_3O_{11}Si$ $[M+Na]^+$ 852.44371, found 852.44378; $[\alpha]_D^{20}$ = -32.3 (c = 2.4, $CHCl_3$).

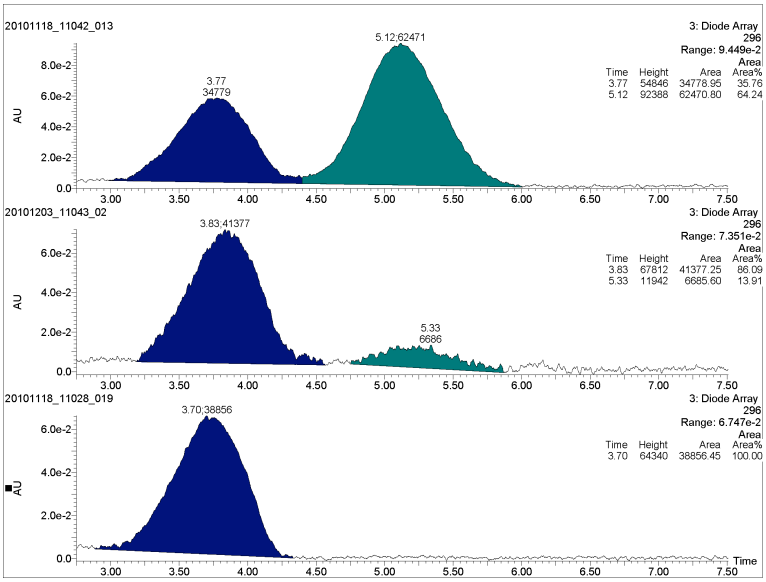


***tert*-Butyl (((10*R*,11*R*,*E*)-6-(diethoxy(methyl)silyl)-13-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-11-methyl-16-nitro-14-oxo-2,3,4,5,8,10,11,12,13,14-decahydrobenzo[*b*][1,9,5]dioxaazacyclohexadecin-10-yl)methyl)(methyl)carbamate (32)**

Z/*E* ratio is 14:86. Yield 44% (pale yellow oil); IR (neat, cm^{-1}) 2972, 2934, 1689, 1636, 1612, 1588, 1515, 1463, 1391, 1365, 1340, 1273, 1252, 1164, 1104, 1078; HRMS (ESI-TOF) calcd. for $C_{41}H_{63}N_3O_{11}Si$ $[M+H]^+$ 802.43046, found 802.42662; $[\alpha]_D^{22}$ = -29.8 (c = 3.2, $CHCl_3$).

The simple diolefinic substrate was synthesized and subjected to RCM reaction using catalyst **A**. A mixture of both stereoisomers was obtained. The *Z*/*E* ratio was analyzed to be 36:64 using SFC/MS chromatography (Figure **I-4**, first trace). SFC: Chiralpak® AD-H column; 25% ^{i}PrOH, 75% sfCO2, 10 minutes run length, $t_R^{(Z)}$ = 3.77 min, area = 36%, $t_R^{(E)}$ = 5.12 min, area = 64%.

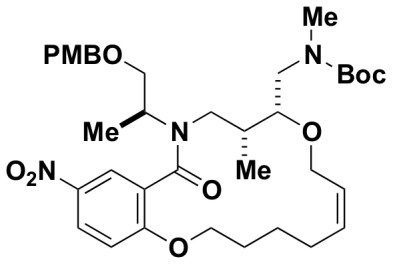
Figure I-4. SFC/MS chromatography of product **45** obtained from different route.



First trace: RCM of simple diolefinic substrate; second trace: protodesilylation of compound **32**; third trace: protodesilylation of compound **31**.

In order to confirm the geometry of the double bond within alkenyl siloxane products **31** and **32**, protodesilylation reaction was performed to generate the simple olefins. The *Z*/*E* ratio of desilylated product **45-*Z*** from compound **31** was larger than 99:1 (Figure **I-4**, third trace, $t_R^{(Z)}$ = 3.70 min, area = 100%). Due to highly rotameric nature of compound **45-*Z***, VT NMR was performed in C_6D_6 at 80 °C. The coupling constant was measured to be 10.5 Hz, characteristic of *Z* olefin. Since the protodesilylation reaction is stereospecific, the configuration of compound **31** was *E*. The *Z*/*E* ratio of desilylated product from compound **32** was 86:14 (Figure **I-4**, second trace, $t_R^{(Z)}$ = 3.83 min, area = 86%, $t_R^{(E)}$ = 5.33 min, area = 14%), which indicated that the *Z*/*E* ratio of compound **32** is 14:86. In both cases, the siloxyl group was able to overcome the intrinsic selectivity

favoring the formation of the *E* olefin. However, the positions of the siloxyl group had different influences on the selectivity of the olefin geometry within the product.



***tert*-Butyl (((10*R*,11*R*,*Z*)-13-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-11-methyl-16-nitro-14-oxo-2,3,4,5,8,10,11,12,13,14-decahydrobenzo[*b*][1,9,5]dioxaazacyclohexadecin-10-yl)methyl)(methyl)carbamate (45-*Z*)**

Yield 86% (pale yellow oil); IR (neat, cm^{-1}) 2936, 2862, 1690, 1633, 1588, 1515, 1464, 1392, 1366, 1341, 1272, 1250, 1159, 1104, 1036, 979; HRMS (ESI-TOF) calcd. for $C_{36}H_{51}N_3O_9$ $[M+Na]^+$ 692.35175, found 692.35064; $[\alpha]_D^{21}$ = -9.9 (c = 4.6, $CHCl_3$).

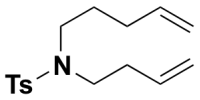
Protodesilylation of **32** generated **45** with 60% yield

G. Influence of the silyl group on the specificity and stereoselectivity of RCM reactions

RCM of simple di-olefinic substrates: substrate (1 equiv.) was dissolved in anhydrous toluene (or other solvent when indicated) at a concentration of 2 mM under argon. Catalyst **A** (20 mol%) or Grubbs II 10 mol%, and 20 mol% 1,4-benzoquinone was added to the solution. High vacuum was applied to the reaction flask for 5 min and charged with

argon. This operation cycle was repeated for 5 times. The reaction was then heated up to 35 °C and left for 12 hours. The resulting mixture was concentrated *in vacuo* and the residue was analyzed by ^{1}H NMR or purified by silica gel column chromatography using Hexanes/EtOAc as eluent.

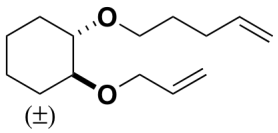
Simple di-olefinic substrates were synthesized and subjected to two different reaction conditions: **I**, 20 mol% cat. **A**, 20 mol% 1,4-benzoquinone, toluene, 2 mM, 35 °C, 12 hours; **II**, 10 mol% Grubbs II, 20 mol% 1,4-benzoquinone, toluene, 2 mM, 35 °C, 12 hours. The reaction outcome was analyzed by proton NMR study of the crude mixture using $CDCl_3$ or C_6D_6 as solvent. Since the outcomes under both conditions are very similar, only expanded region of the proton NMR spectrum from condition **II** was shown here. The resonance of the olefinic proton corresponding to the *cis* olefin was known from the protodesilylation of alkenyl siloxane intermediate. The resonance of the olefinic proton corresponding to the *trans* olefin was rigorously analyzed when the reaction is *trans* selective



***N*-(but-3-en-1-yl)-4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide (33')**

IR (neat, cm^{-1}) 3077, 2977, 2929, 2869, 1641, 1599, 1494, 1458, 1340, 1158, 1091, 993, 958; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 5.80-5.66 (m, 2 H), 5.06-4.96 (m, 4 H), 3.16 (t, *J* = 7.5 Hz, 2 H), 3.11 (t, *J* = 7.5 Hz, 2 H), 2.41 (s, 3 H), 2.28 (dt, *J* = 7.3, 7.3 Hz, 2 H), 2.04 (dt, *J* = 7.1, 7.1 Hz, 2 H), 1.63 (tt, *J* = 7.5, 7.5 Hz, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.0, 137.4, 136.9, 134.6, 129.6,

127.1, 117.0, 115.2, 47.9, 47.7, 33.3, 30.7, 27.8, 21.4; HRMS (ESI-TOF) calcd. for $C_{16}H_{23}NO_2S$ $[M+Na]^+$ 316.13417, found 316.13501.



(±)

(1*S*,2*S*)-1-(allyloxy)-2-(pent-4-en-1-yloxy)cyclohexane and its enantiomer (34')

IR (neat, cm^{-1}) 3078, 2934, 2861, 1642, 1450, 1366, 1315, 1271, 1243, 1208, 1161, 1106, 993; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.97-5.89 (m, 1 H), 5.86-5.78 (m, 1 H), 5.29-5.26 (m, 1 H), 5.14-5.12 (m, 1 H), 5.04-5.00 (m, 1 H), 4.96-4.94 (m, 1 H), 4.16-4.10 (m, 2 H), 3.60-3.52 (m, 2 H), 3.23-3.14 (m, 2 H), 2.15-2.11 (m, 2 H), 1.98-1.95 (m, 2 H), 1.68-1.62 (m, 4 H), 1.31-1.17 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.5, 135.8, 116.1, 114.5, 81.5, 80.8, 71.0, 69.2, 30.4, 30.2, 29.5, 23.6, 23.6; HRMS (ESI-TOF) calcd. for $C_{14}H_{24}O_2$ $[M+Na]^+$ 247.16685, found 247.16675.

Figure I-5. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **33'** under condition II.

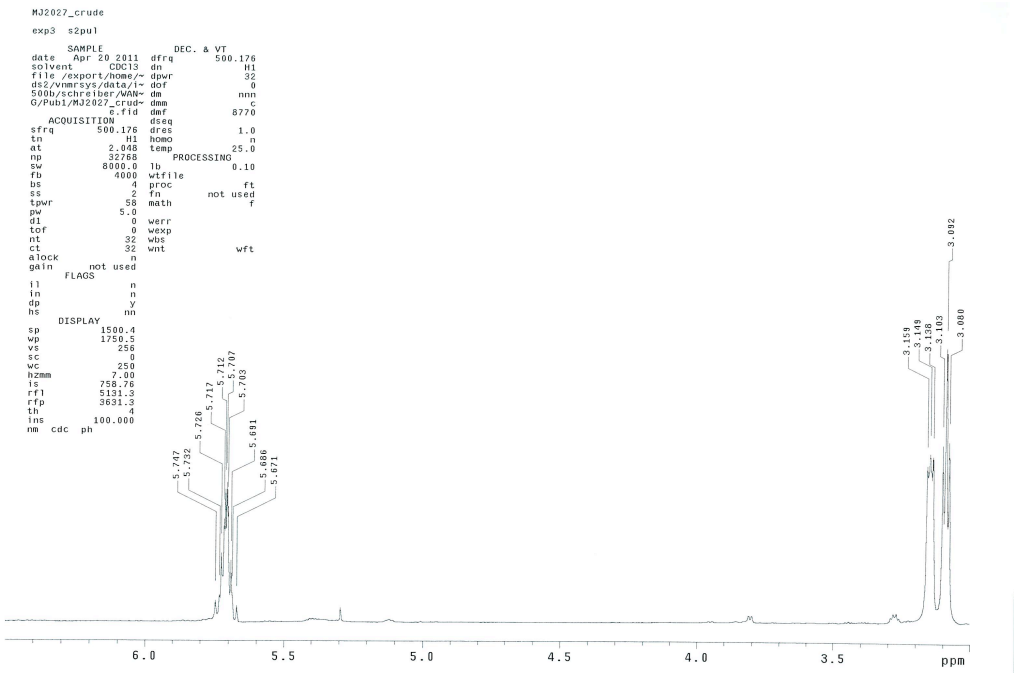
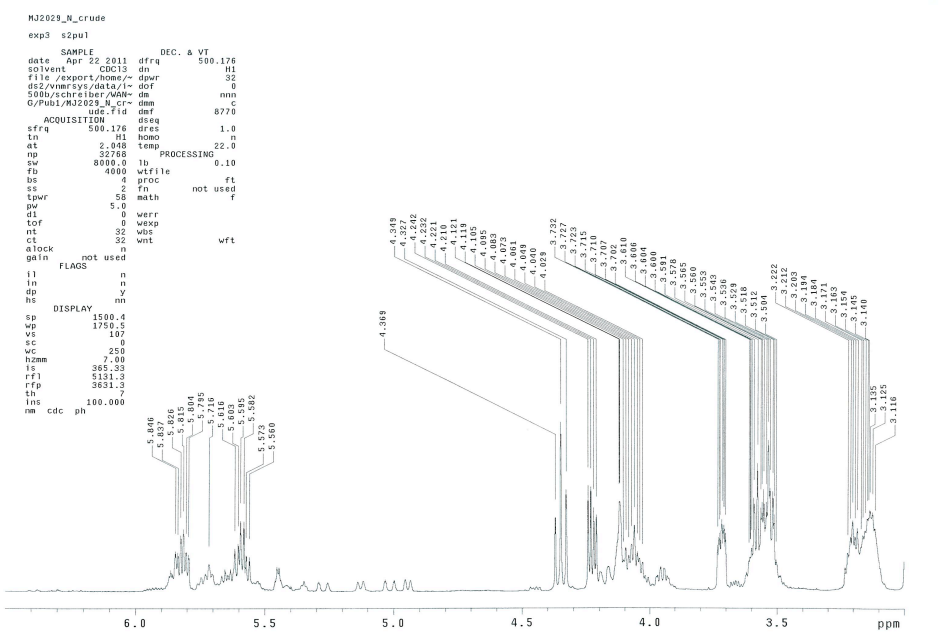
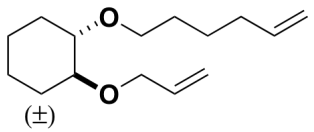


Figure I-6. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **34'** under condition II.



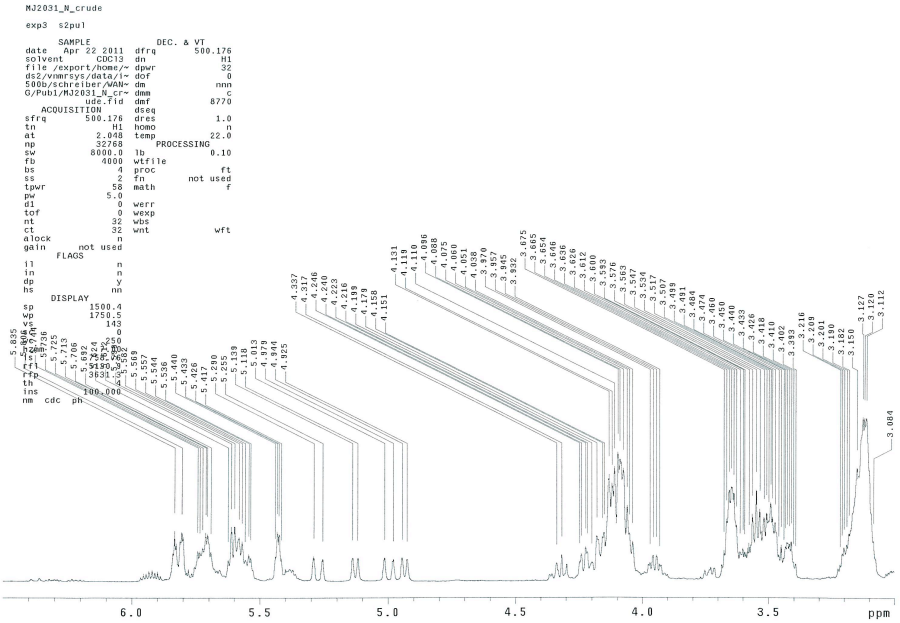


(±)

(1*S*,2*S*)-1-(allyloxy)-2-(hex-5-en-1-yloxy)cyclohexane and its enantiomer (35')

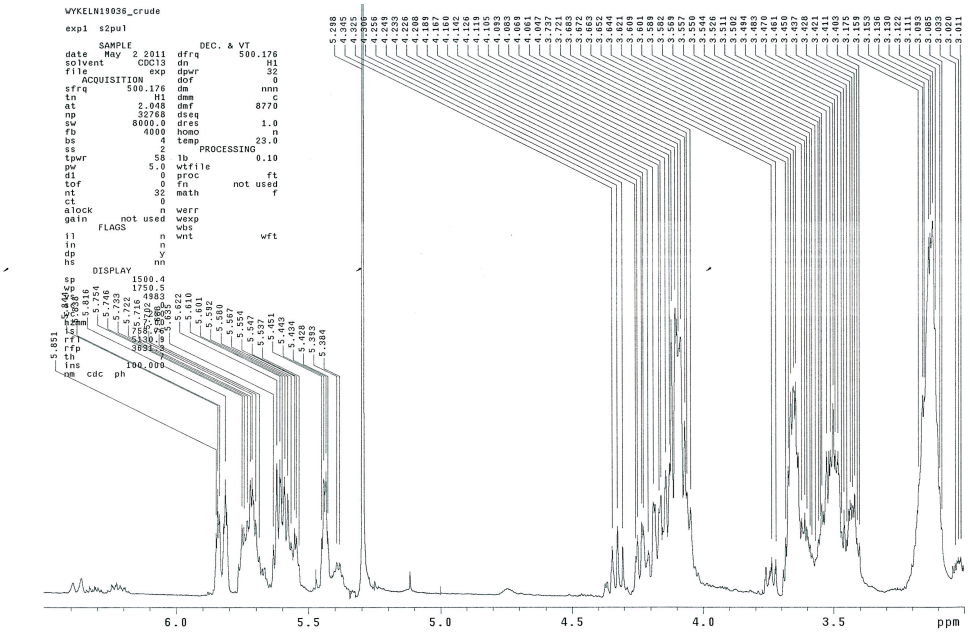
IR (neat, cm^{-1}) 3077, 2933, 1642, 1450, 1366, 1244, 1098; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.97-5.89 (m, 1 H), 5.85-5.77 (m, 1 H), 5.29-5.26 (m, 1 H), 5.14-5.12 (m, 1 H), 5.01-4.98 (m, 1 H), 4.95-4.93 (m, 1 H), 4.16-4.08 (m, 2 H), 3.59-3.51 (m, 2 H), 3.22-3.14 (m, 2 H), 2.06 (ddd, *J* = 7.0, 7.0, 7.0 Hz, 2 H), 1.97-1.95 (m, 2 H), 1.64-1.55 (m, 4 H), 1.49-1.43 (m, 2 H), 1.31-1.17 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.9, 135.8, 116.1, 114.4, 81.5, 80.8, 71.1, 69.8, 33.4, 30.4, 30.2, 29.8, 25.5, 23.6, 23.6; HRMS (ESI-TOF) calcd. for $C_{15}H_{26}O_2$ $[M+Na]^+$ 261.18250, found 261.18388.

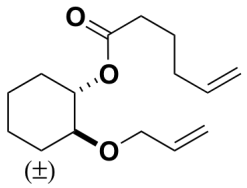
Figure I-7. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **35'** under condition II.



The monocyclized *Z*-alkene compound **35-*Z*** (corresponding to what would be the monocyclized product of the RCM of **35'**) obtained from protodesilylation of compound **16** was subjected to reaction condition II using second generation Grubbs catalyst. It was almost completely consumed to generate dimers and oligomers (Figure **I-8**).

Figure I-8. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **35-*Z*** under condition II.





(1*S*,2*S*)-2-(allyloxy)cyclohexyl hex-5-enoate and its enantiomer (36')

IR (neat, cm^{-1}) 3078, 2938, 2863, 1734, 1642, 1453, 1367, 1246, 1175, 1101, 994; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.90-5.74 (m, 2 H), 5.26-5.23 (m, 1 H), 5.13-5.11 (m, 1 H), 5.04-4.96 (m, 2 H), 4.80-4.75 (m, 1 H), 4.10-4.06 (m, 1 H), 4.02-3.98 (m, 1 H), 3.29 (ddd, J = 8.5, 8.5, 4.0 Hz, 1 H), 2.31 (dd, J = 7.2, 7.2 Hz, 2 H), 2.09 (ddd, J = 7.0, 7.0, 7.0 Hz, 2 H), 2.00-1.97 (m, 2 H), 1.76-1.63 (m, 4 H), 1.40-1.20 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.9, 137.8, 135.3, 116.2, 115.2, 78.4, 74.8, 70.4, 33.9, 33.0, 29.9, 29.8, 24.1, 23.2; HRMS (ESI-TOF) calcd. for $C_{15}H_{24}O_3$ $[M+Na]^+$ 275.16177, found 275.16271.

Figure I-9. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **36'** under condition II.

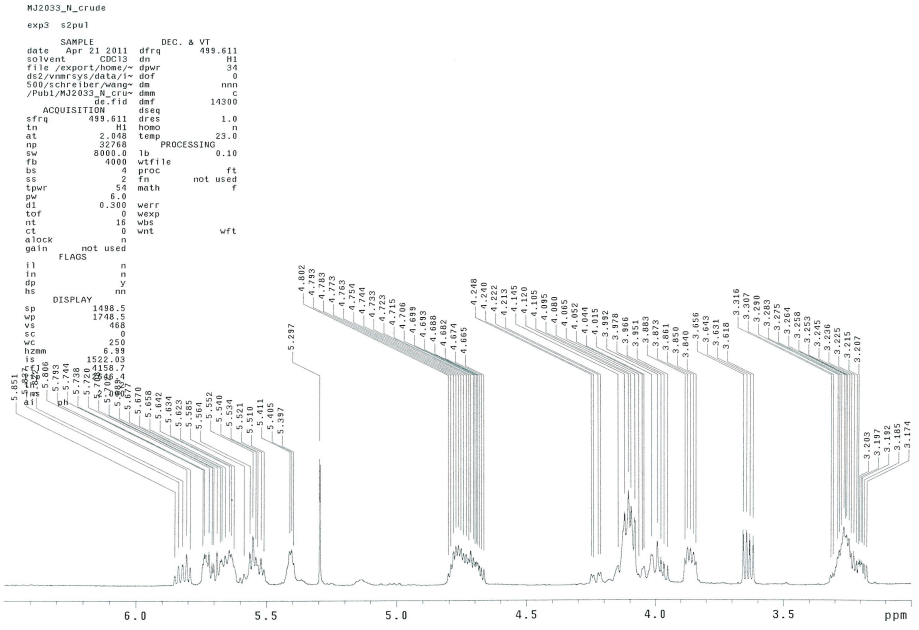
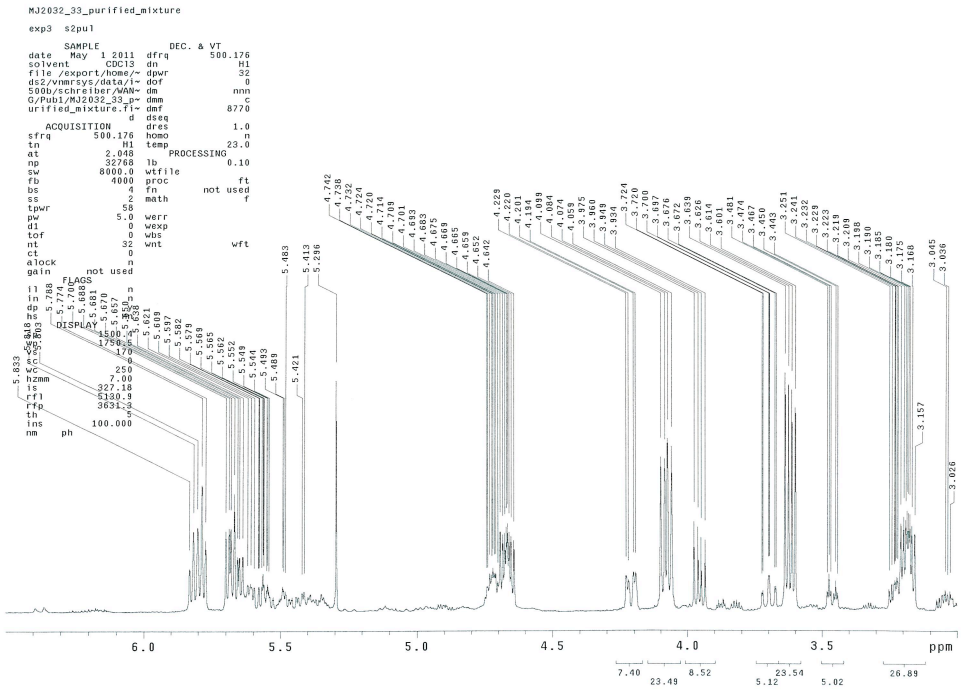
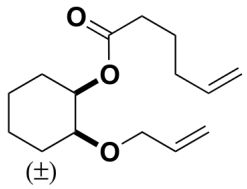


Figure I-10. ^{1}H NMR spectrum of purified monocyclized product mixture from reaction of **36'** for ratio determination.

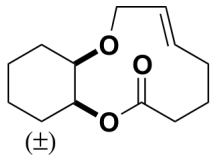




(1*R*,2*S*)-2-(allyloxy)cyclohexyl hex-5-enoate and its enantiomer (37')

IR (neat, cm^{-1}) 3078, 2939, 2861, 1732, 1642, 1450, 1363, 1247, 1175, 1089, 994; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.91-5.83 (m, 1 H), 5.80-5.73 (m, 1 H), 5.27-5.23 (m, 1 H), 5.14-5.11 (m, 1 H), 5.10-5.08 (m, 1 H), 5.03-4.96 (m, 2 H), 4.04 (dd, *J* = 13.0, 5.5 Hz, 1 H), 3.97 (dd, *J* = 13.0, 5.7 Hz, 1 H), 3.47-3.46 (m, 1 H), 2.34 (dd, *J* = 7.5, 7.5 Hz, 2 H), 2.11-2.07 (m, 2 H), 1.90-1.85 (m, 1 H), 1.81-1.64 (m, 4 H), 1.60-1.46 (m, 3 H), 1.42-1.27 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.1, 137.8, 135.2, 116.5, 115.2, 76.0, 70.9,

69.6, 33.9, 33.0, 27.9, 27.8, 24.2, 22.1, 21.6; HRMS (ESI-TOF) calcd. for $C_{15}H_{24}O_3$ $[M+Na]^+$ 275.16177, found 275.16316.

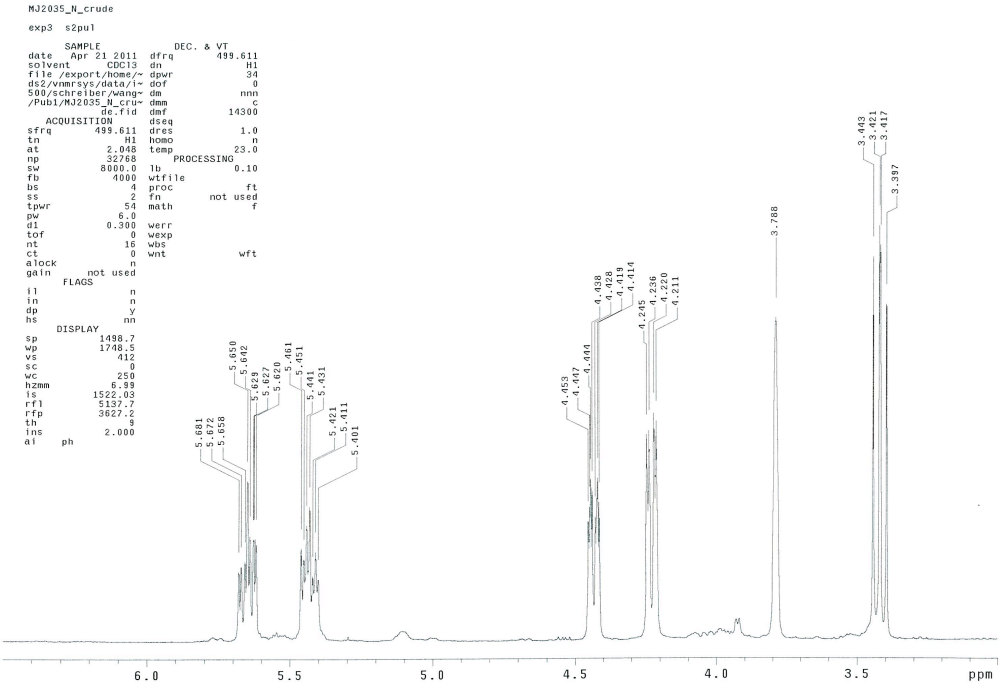


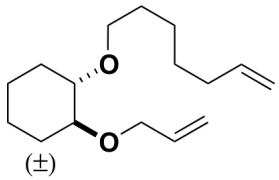
(±)

(9a*R*,13a*S*,*E*)-3,4,5,8,9a,10,11,12,13,13a-decahydro-2*H*-benzo[*b*][1,4]dioxacycloundecin-2-one and its enantiomer (37-*E*)

Yield 73% (colorless oil); IR (neat, cm^{-1}) 2934, 2858, 1725, 1443, 1363, 1256, 1210, 1159, 1139, 1109, 1089, 1073, 1047, 980; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.64 (ddd, *J* = 15.0, 10.5, 4.0 Hz, 1 H), 5.42 (ddd, *J* = 15.0, 10.2, 5.5 Hz, 1 H), 4.44-4.40 (m, 1 H), 4.23-4.20 (dd, *J* = 13.0, 4.2 Hz, 1 H), 3.77 (bs, 1 H), 3.40 (dd, *J* = 12.5, 11.0 Hz, 1 H), 2.38-2.29 (m, 2 H), 2.12-2.07 (m, 1 H), 1.99-1.70 (m, 6 H), 1.56-1.47 (m, 2 H), 1.41-1.23 (m, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.9, 132.0, 132.0, 75.1, 74.9, 72.2, 34.4, 33.6, 30.6, 25.8, 24.5, 24.2, 19.4; HRMS (ESI-TOF) calcd. for $C_{13}H_{20}O_3$ $[M+H]^+$ 225.14852, found 225.16079.

Figure I-11. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **37'** under condition II (the major product was purifiable and is reported as **37-*E***).





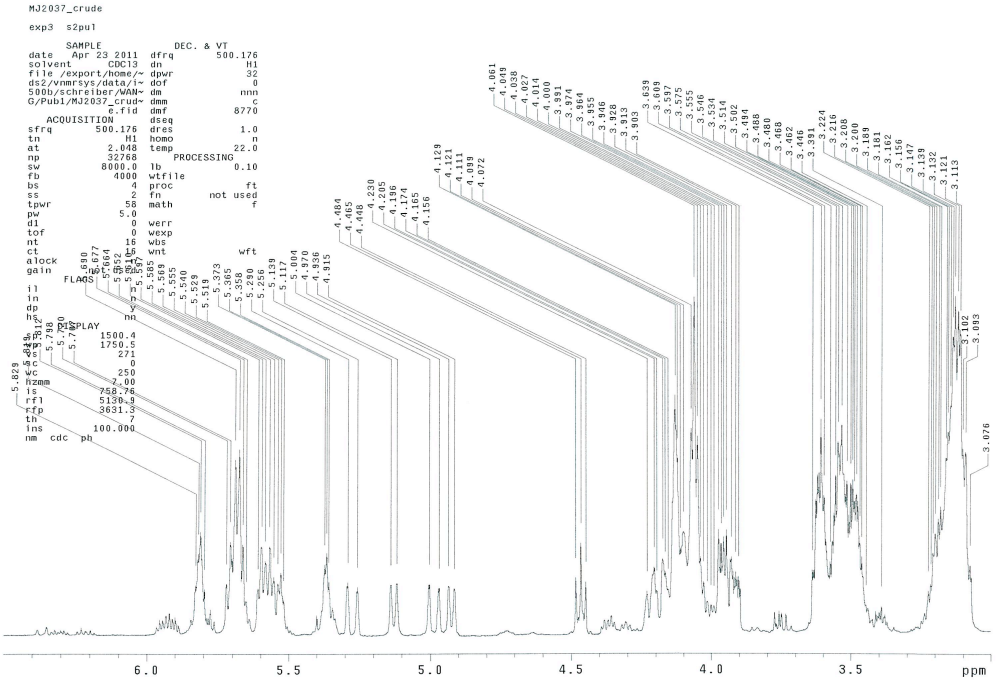
(±)

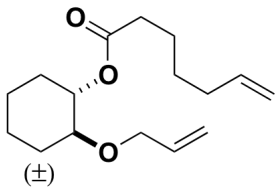
(1*S*,2*S*)-1-(allyloxy)-2-(hept-6-en-1-yloxy)cyclohexane and its enantiomer (39')

IR (neat, cm^{-1}) 3077, 2932, 2859, 1642, 1451, 1365, 1314, 1270, 1244, 1208, 1161, 1107, 994; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.97-5.89 (m, 1 H), 5.84-5.76 (m, 1 H), 5.29-5.25 (m, 1 H), 5.14-5.12 (m, 1 H), 5.01-4.97 (m, 1 H), 4.94-4.91 (m, 1H), 4.16-4.08 (m, 2 H), 3.59-3.50 (m, 2 H), 3.22-3.13 (m, 2 H), 2.07-2.03 (m, 2 H), 1.96-1.95 (m, 2 H), 1.65-1.54 (m, 4 H), 1.44-1.33 (m, 4 H), 1.30-1.15(m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 139.0,

135.8, 116.0, 114.2, 81.6, 80.8, 71.1, 69.9, 33.7, 30.4, 30.2, 30.2, 28.8, 25.7, 23.6, 23.6; HRMS (ESI-TOF) calcd. for $C_{16}H_{28}O_2$ $[M+Na]^+$ 275.19815, found 275.19975.

Figure I-12. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **39'** under condition II.



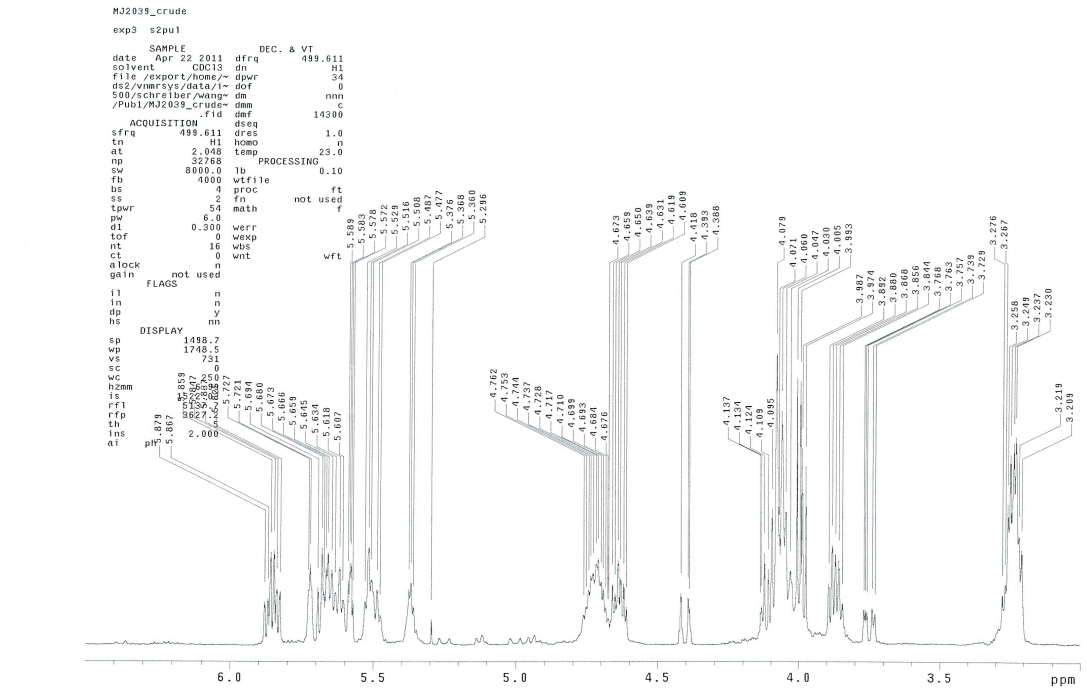


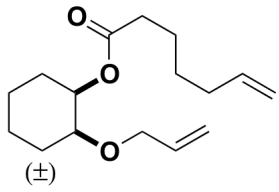
(1*S*,2*S*)-2-(allyloxy)cyclohexyl hept-6-enoate and its enantiomer (40')

IR (neat, cm^{-1}) 3078, 2937, 2863, 1735, 1641, 1453, 1353, 1174, 1101, 994; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.90-5.74 (m, 2 H), 5.26-5.23 (m, 1 H), 5.13-5.11 (m, 1 H), 5.01-4.98 (m, 1 H), 4.95-4.93 (m, 1 H), 4.77 (ddd, *J* = 8.5, 8.5. 5.0 Hz, 1 H), 4.08 (dd, *J* = 7.8,

5.0 Hz, 1 H), 4.00 (dd, *J* = 7.8, 5.0 Hz, 1 H), 3.29 (ddd, *J* = 8.5, 8.5, 4.0 Hz, 1 H), 2.30 (dd, *J* = 7.2, 7.2 Hz, 2 H), 2.08-2.04 (m, 2 H), 1.99-1.97 (m, 2 H), 1.70-1.61 (m, 4 H), 1.46-1.20 (m, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.0, 138.4, 135.3, 116.2, 114.6, 78.5, 74.8, 70.4, 34.5, 33.4, 29.9, 29.8, 28.3, 24.5, 23.2; HRMS (ESI-TOF) calcd. for $C_{16}H_{26}O_3$ $[M+Na]^+$ 289.17742, found 289.17766.

Figure I-13. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **40'** under condition II.





(1*R*,2*S*)-2-(allyloxy)cyclohexyl hept-6-enoate and its enantiomer (41')

IR (neat, cm^{-1}) 3078, 2938, 2860, 1732, 1642, 1450, 1362, 1236, 1174, 1089, 994; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.91-5.75 (m, 2 H), 5.27-5.23 (m, 1 H), 5.14-5.08 (m, 2 H), 5.02-4.98 (m, 1 H), 4.95-4.93 (m, 1 H), 4.04 (dd, *J* = 8.0, 5.5 Hz, 1 H), 3.98 (dd, *J* = 8.0, 5.5 Hz, 1 H), 3.48-3.46 (m, 1 H), 2.34 (dd, *J* = 7.2, 7.2 Hz, 2 H), 2.08-2.04 (m, 2 H), 1.90-1.85 (m, 1 H), 1.81-1.75 (m, 1 H), 1.70-1.28 (m, 10 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.2, 138.5, 135.2, 116.5, 114.6, 76.0, 71.0, 69.6, 34.5, 33.4, 28.3, 27.9, 27.8, 24.5, 22.1, 21.7; HRMS (ESI-TOF) calcd. for $C_{16}H_{26}O_3$ $[M+Na]^+$ 289.17742, found 289.17867.

Figure I-14. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **41'** under condition II.

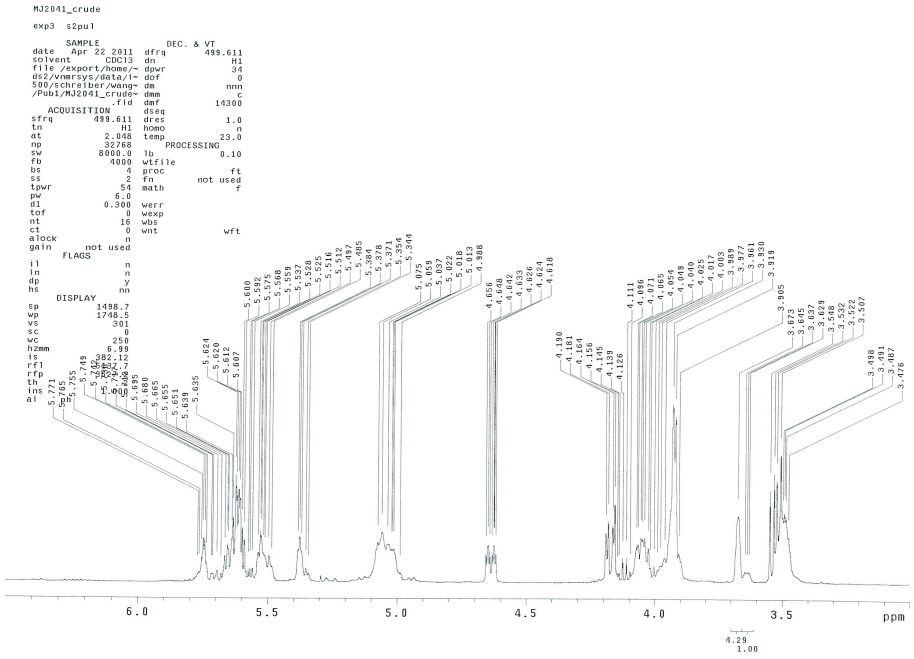
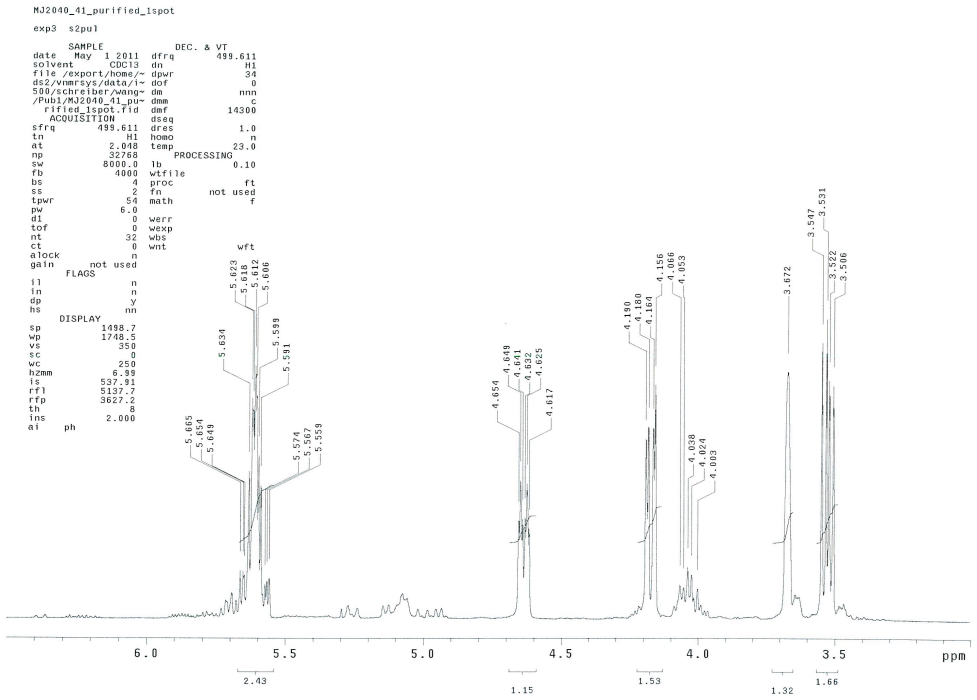
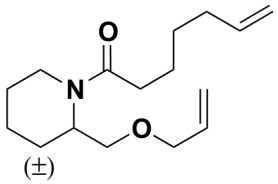


Figure I-15. ^{1}H NMR spectrum of purified monocyclized product mixture from reaction of **41'** for identification of *trans* isomer.



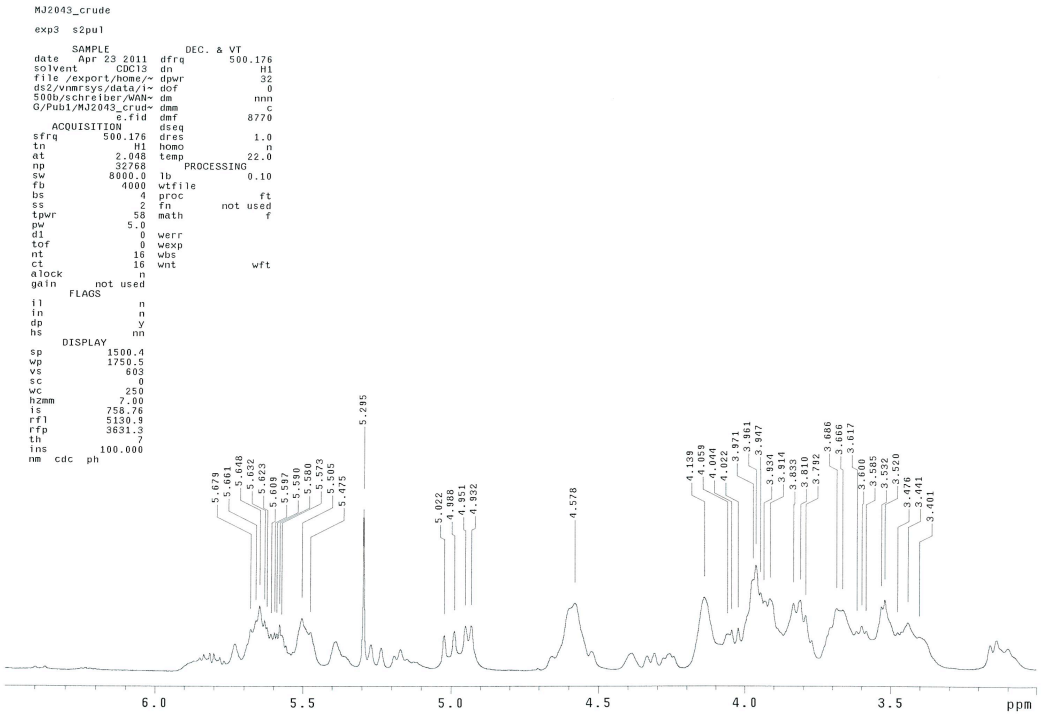


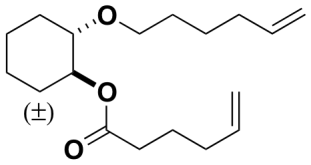
(±)

(±)-1-(2-((allyloxy)methyl)piperidin-1-yl)hept-6-en-1-one (38')

IR (neat, cm^{-1}) 3076, 2934, 2859, 1642, 1426, 1357, 1243, 1178, 1134, 1104, 1057, 1028, 992; The ^{1}H and ^{13}C NMR spectra of many of this compound was complicated owing to the combination of rotamers. HRMS (ESI-TOF) calcd. for $C_{16}H_{27}NO_2$ $[M+Na]^+$ 288.19340, found 288.19396.

Figure I-16. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **38'** under condition II.



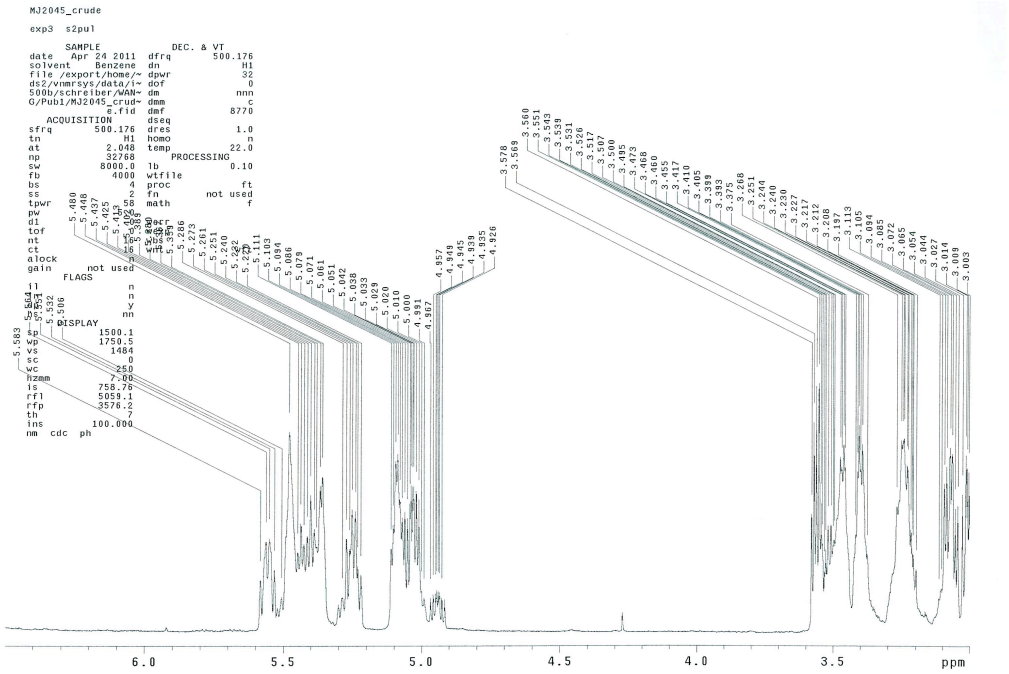


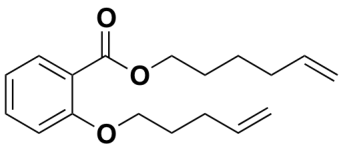
(1*S*,2*S*)-2-(hex-5-en-1-yloxy)cyclohexyl hex-5-enoate and its enantiomer (43')

IR (neat, cm^{-1}) 3077, 2936, 2862, 1734, 1641, 1453, 1369, 1175, 1111; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.83-5.74 (m, 2 H), 5.04-4.92 (m, 4 H), 4.75 (ddd, *J* = 9.0, 9.0, 4.5 Hz, 1 H), 3.54 (ddd, *J* = 9.0, 6.5, 6.5 Hz, 1 H), 3.40 (ddd, *J* = 9.0, 6.5, 6.5 Hz, 1 H), 3.21 (ddd, *J* = 8.5, 8.5, 4.0 Hz, 1 H), 3.32-2.29 (m, 2 H), 2.11-2.02 (m, 4 H), 2.00-1.95 (m, 2 H), 1.76-1.63 (m, 4 H), 1.56-1.50 (m, 2 H), 1.46-1.38 (m, 2 H), 1.37-1.19(m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.9, 138.8, 137.8, 115.2, 114.4, 79.0, 74.7, 69.3, 33.9, 33.5, 33.0, 29.8,

29.6, 25.5, 24.2, 23.3; HRMS (ESI-TOF) calcd. for $C_{18}H_{30}O_3$ $[M+Na]^+$ 317.20872, found 317.20928.

Figure I-17. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **43'** under condition II.





Hex-5-en-1-yl 2-(pent-4-en-1-yloxy)benzoate (**14'**)

IR (neat, cm^{-1}) 3077, 2976, 2940, 2870, 1728, 1704, 1641, 1601, 1583, 1491, 1469, 1452, 1416, 1386, 1302, 1251, 1164, 1133, 1080, 1049, 1013, 995; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1 H), 7.44-7.41 (m, 1 H), 6.98-6.94 (m, 2 H), 5.89-5.77 (m, 2 H), 5.08-4.95 (m, 4 H), 4.30 (t, J = 7.0 Hz, 2 H), 4.04 (t, J = 6.5 Hz, 2 H), 2.30-2.25 (m, 2 H),

2.14-2.09 (m, 2 H), 1.96-1.90 (m, 2 H), 1.80-1.74 (m, 2 H), 1.58-1.52 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.7, 158.4, 138.4, 137.7, 133.1, 131.5, 120.9, 120.0, 115.2, 114.8, 113.1, 68.0, 64.7, 33.3, 30.0, 28.3, 28.2, 25.3; HRMS (ESI-TOF) calcd. for $C_{18}H_{24}O_3$ $[M+Na]^+$ 311.16177, found 311.16440.

Figure I-18. ^{1}H NMR spectrum of purified monocyclized product mixture from reaction of **43'** for ratio determination.

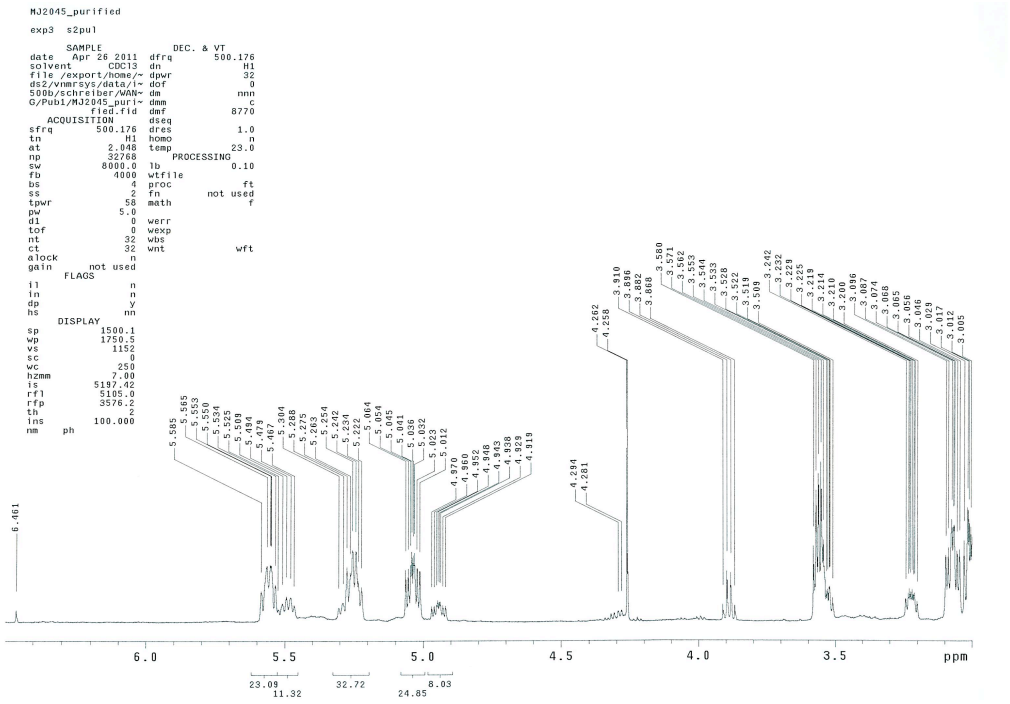
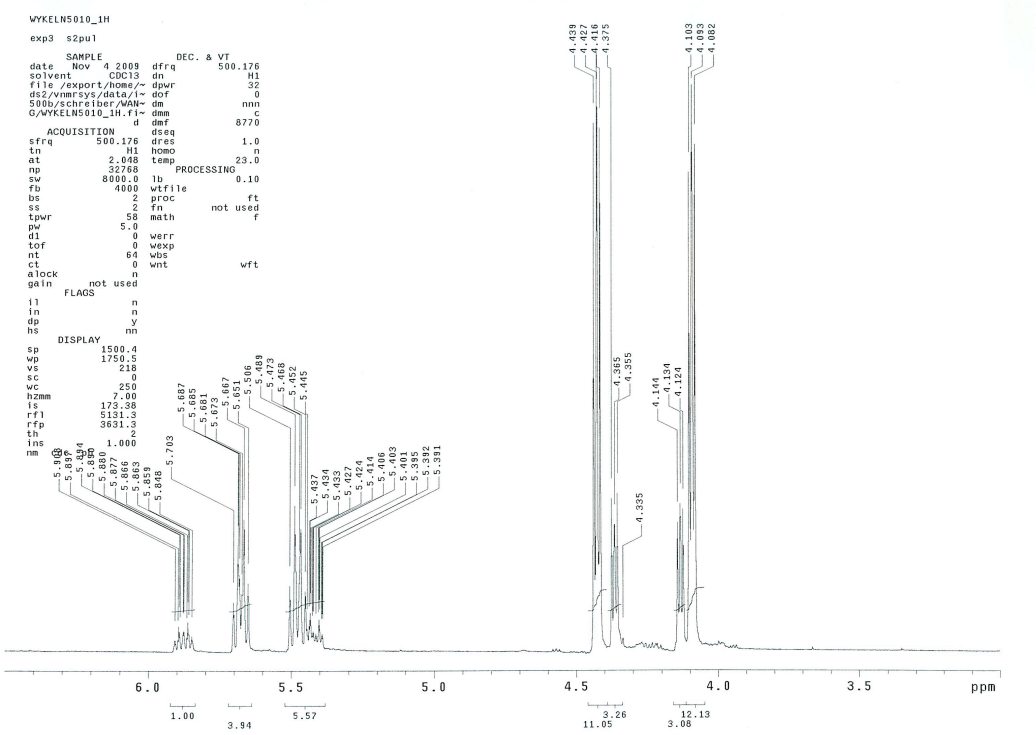
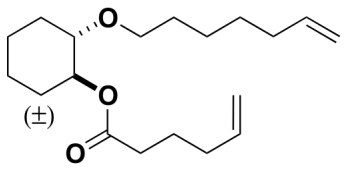


Figure I-19. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **14'** under condition II.



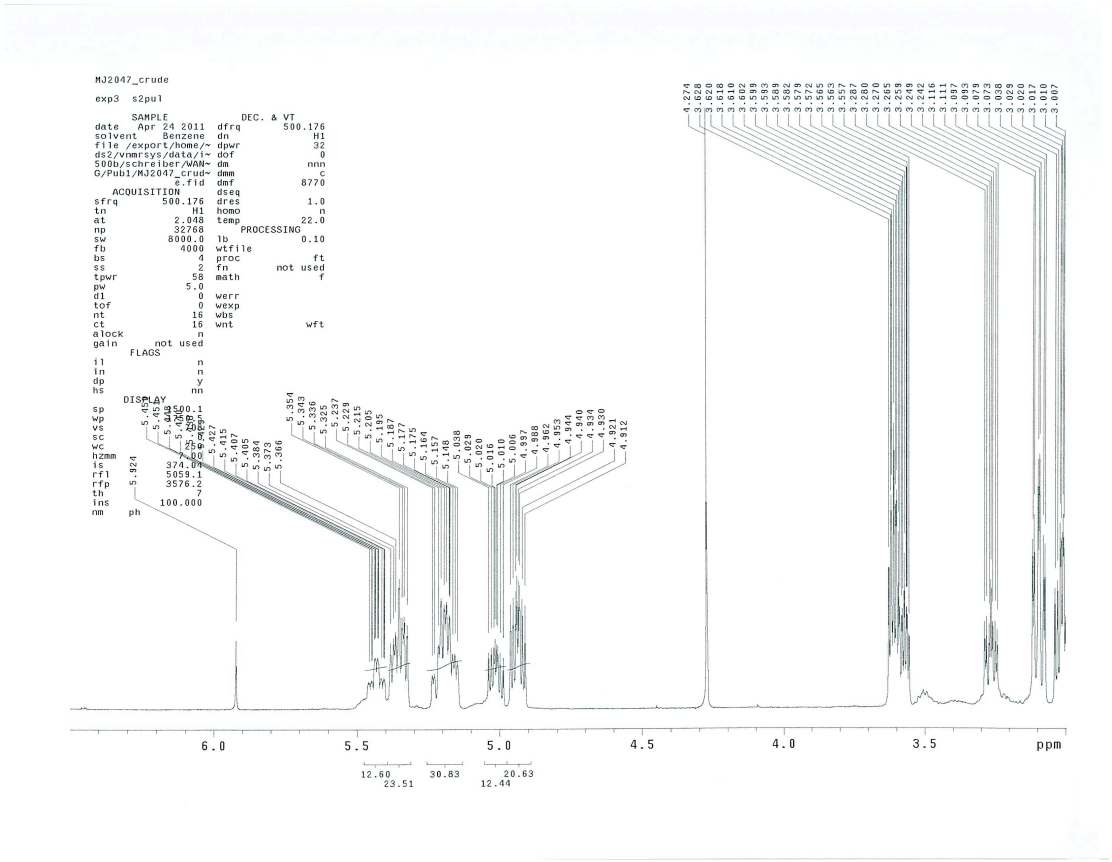


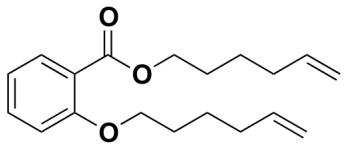
(1*S*,2*S*)-2-(hept-6-en-1-yloxy)cyclohexyl hex-5-enoate and its enantiomer (44')

IR (neat, cm^{-1}) 3077, 2934, 2861, 1734, 1641, 1452, 1417, 1369, 1247, 1175, 1111, 1026, 994; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.83-5.74 (m, 2 H), 5.04-4.91 (m, 4 H), 4.75 (ddd, *J* = 9.0, 9.0, 4.5 Hz, 1 H), 3.53 (ddd, *J* = 9.5, 6.5, 6.5 Hz, 1 H), 3.39 (ddd, *J* = 9.0, 7.0, 7.0 Hz, 1 H), 3.20 (ddd, *J* = 9.0, 9.0, 4.0 Hz, 1 H), 2.32-2.29 (m, 2 H), 2.11-2.07 (m, 2 H), 2.05-2.01 (m, 2 H), 1.99-1.95 (m, 2 H), 1.76-1.63 (m, 4 H), 1.54-1.49 (m, 2 H), 1.41-1.19 (m, 8 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.9, 138.9, 137.8, 115.2, 114.2, 79.0, 74.8,

69.5, 33.9, 33.7, 33.0, 30.0, 29.8, 28.7, 25.6, 24.2, 23.3; HRMS (ESI-TOF) calcd. for $C_{19}H_{32}O_3$ $[M+H]^+$ 309.24242, found 309.24229.

Figure I-20. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **44'** under condition II.



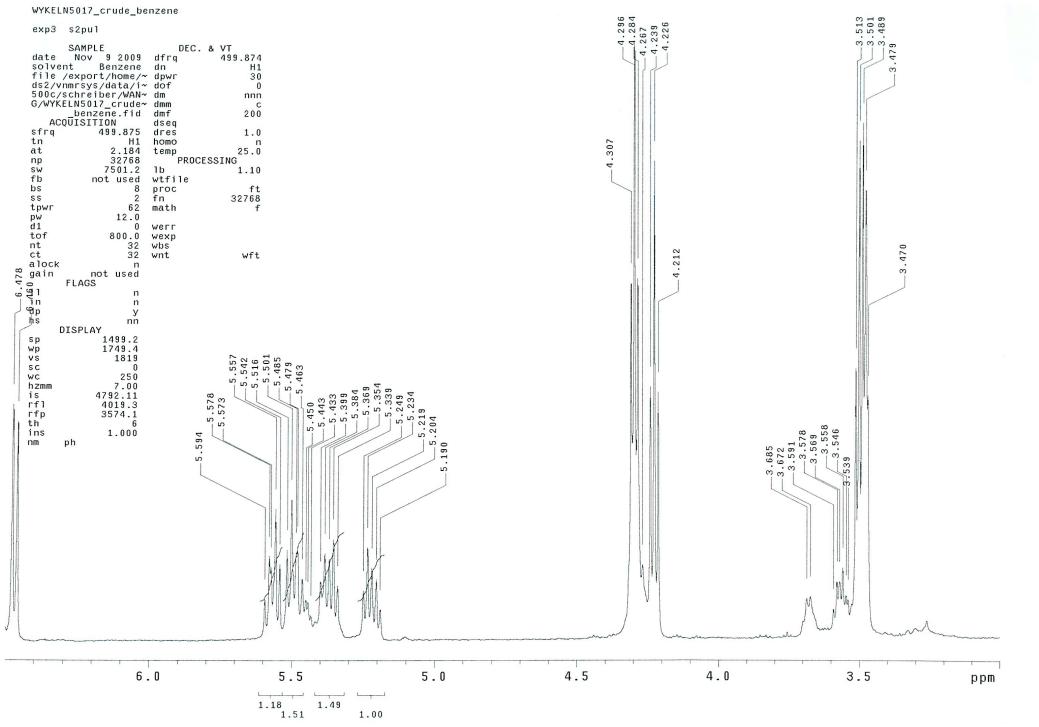


Hex-5-en-1-yl 2-(hex-5-en-1-yloxy)benzoate (**42'**)

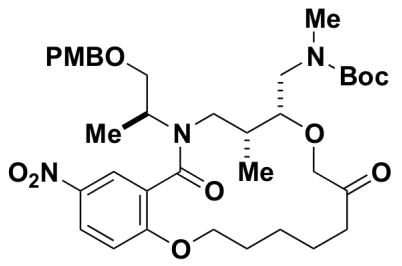
IR (neat, cm^{-1}) 3076, 2937, 2862, 1728, 1704, 1640, 1601, 1583, 1491, 1469, 1453, 1386, 1302, 1250, 1164, 1133, 1079, 1049, 995, 953; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.78-7.76

(m, 1 H), 7.44-7.41 (m, 1 H), 6.97-6.94 (m, 2 H), 5.87-5.78 (m, 2 H), 5.05-5.01 (m, 2 H), 4.98-4.96 (m, 2 H), 4.30 (t, J = 6.8 Hz, 2 H), 4.03 (t, J = 6.5 Hz, 2 H), 2.15-2.10 (m, 4 H), 1.85 (tt, J = 7.1, 7.1 Hz, 2 H), 1.77 (tt, J = 7.2, 7.2 Hz, 2 H), 1.63-1.52 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 166.7, 158.4, 138.5, 138.4, 133.1, 131.5, 120.8, 120.0, 114.8, 114.7, 113.0, 68.6, 64.7, 33.4, 33.3, 28.6, 28.2, 25.3, 25.2; HRMS (ESI-TOF) calcd. for $C_{19}H_{26}O_3$ $[M+Na]^+$ 325.17742, found 325.17910.

Figure I-21. ^{1}H NMR spectrum (expansion of 3.0 to 6.5ppm) of reaction mixture of **42'** under condition II.



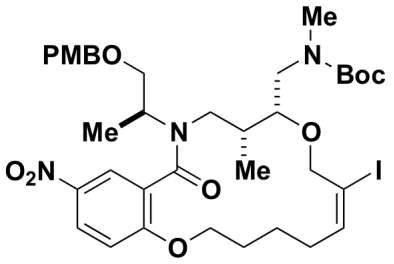
H. Further transformation of macrocyclic alkenylsiloxanes



***tert*-Butyl (((10*R*,11*R*)-13-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-11-methyl-16-nitro-7,14-dioxo-2,3,4,5,6,7,8,10,11,12,13,14-dodecahydrobenzo[*b*][1,9,5]dioxaazacyclohexadecin-10-yl)methyl)(methyl)carbamate (47)**

Adapted from the reported procedure,[244] to a stirred solution of compound **31** (78.0 mg, 0.097 mmol) in tetrahydrofuran/methanol (1:1, 2.0 mL, 50 mM), was added anhydrous potassium fluoride (17.0 mg, 0.29 mmol), potassium bicarbonate (29.0 mg, 0.15 mmol), and 30% hydrogen peroxide (110 mg, 0.97 mmol). The reaction was stirred at 23 °C for 3 h. The suspension was then filtered through a Celite pad and the filtrate was dried with sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography (gradient 40 – 60% ethyl acetate/hexane) to give compound **47** as a white solid (50.0 mg, 0.073 mmol).

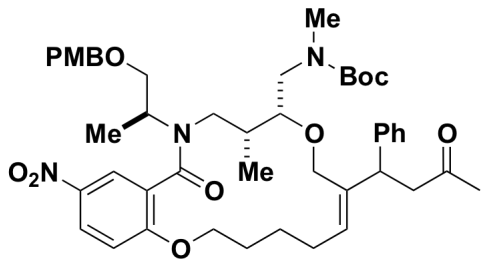
Yield 75%; IR (neat, cm^{-1}) 3055, 2936, 2870, 1729, 1689, 1634, 1613, 1588, 1516, 1489, 1462, 1392, 1366, 1340, 1302, 1271, 1152, 1109, 1035; HRMS (ESI-TOF) calcd. for $C_{36}H_{51}N_3O_{10}$ $[M+Na]^+$ 708.34667, found 708.34659; $[\alpha]_D^{19}$ = -17.5 (c = 2.2, $CHCl_3$).



***tert*-Butyl (((10*R*,11*R*,*E*)-7-iodo-13-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-11-methyl-16-nitro-14-oxo-2,3,4,5,8,10,11,12,13,14-decahydrobenzo[*b*][1,9,5]dioxaazacyclohexadecin-10-yl)methyl)(methyl)carbamate (48)**

To a stirred solution of compound **31** (60.0 mg, 0.075 mmol) in dimethylformamide (3.7 mL, 20 mM), was added anhydrous potassium fluoride (8.7 mg, 0.15 mmol), potassium carbonate (15.0 mg, 0.15 mmol), and iodine (95.0 mg, 0.37 mmol). The reaction was heated to 50 °C and left for 18 hours. Then another portion of potassium fluoride (8.7 mg, 0.15 mmol), potassium carbonate (15.0 mg, 0.15 mmol), and iodine (95.0 mg, 0.37 mmol) was added. The resulting mixture was allowed to react at 50 °C for another 18 hours before quenched with 20 mL solution of 10% sodium bisulfite and 10% sodium bicarbonate. The aqueous solution was extracted with dichloromethane (15 mL x 3). The combined extracts were dried with sodium sulfate and concentrated *in vacuo*. Purification by column chromatography (gradient 20 – 50% ethyl acetate/hexane) gave compound **48** as yellow oil (42.0 mg, 0.053 mmol).

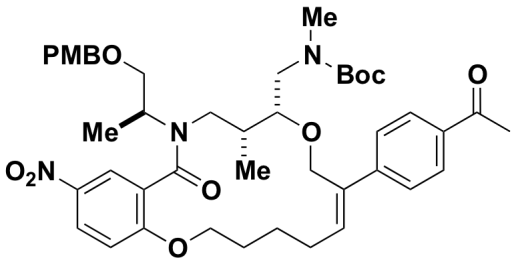
Yield 70%; IR (neat, cm^{-1}) 2968, 2935, 2866, 1687, 1631, 1613, 1588, 1515, 1466, 1392, 1365, 1341, 1302, 1272, 1250, 1158, 1110, 1083, 1034; HRMS (ESI-TOF) calcd. for $C_{36}H_{50}N_3O_9I$ $[M+H]^+$ 796.26645, found 796.26655; $[\alpha]_D^{24}$ = -33.1 (c = 4.1, $CHCl_3$).



***tert*-Butyl (((10*R*,11*R*,*Z*)-13-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-11-methyl-16-nitro-14-oxo-7-(3-oxo-1-phenylbutyl)-2,3,4,5,8,10,11,12,13,14-decahydrobenzo[*b*][1,9,5]dioxaazacyclohexadecin-10-yl)methyl)(methyl)carbamate (50**, mixture of diastereomers**)**

Adapted from the reported procedure,[247,248] to a round bottom flask armed with a condenser, was added compound **31** (77.0 mg, 0.096 mmol), anhydrous tetrahydrofuran (4.8 mL, 20 mM), *trans*-4-phenyl-3-buten-2-one (28.1 mg, 0.192 mmol), cyclooctadiene rhodium chloride dimer (9.5 mg, 0.019 mmol), and tetra-*n*-butylammonium fluoride (1.0 M solution in tetrahydrofuran, 144 μl, 0.14 mmol). The reaction was stirred under reflux for 3 h. The suspension was then concentrated *in vacuo* and purified by column chromatography (gradient 20 – 50% ethyl acetate/hexane) to give compound **50** as yellow oil (38.0 mg, 0.047 mmol).

Yield 48%; IR (neat, cm^{-1}) 2971, 2935, 2866, 1690, 1633, 1613, 1588, 1515, 1482, 1468, 1454, 1393, 1365, 1341, 1302, 1271, 1250, 1157, 1108, 1079, 1035; HRMS (ESI-TOF) calcd. for $C_{46}H_{61}N_3O_{10}$ $[M+H]^+$ 816.44297, found 816.44253; $[\alpha]_D^{22}$ = -31.1 (c = 4.5, $CHCl_3$).



***tert*-Butyl (((10*R*,11*R*,*Z*)-7-(4-acetylphenyl)-13-((*S*)-1-((4-methoxybenzyl)oxy)propan-2-yl)-11-methyl-16-nitro-14-oxo-2,3,4,5,8,10,11,12,13,14-decahydrobenzo[*b*][1,9,5]dioxaazacyclohexadecin-10-yl)methyl)(methyl)carbamate (49)**

Adapted from the reported procedure,[246] to a stirred solution of compound **31** (55.0 mg, 0.069 mmol) in anhydrous tetrahydrofuran (1.4 mL, 20 mM), was added 1-(4-iodophenyl)ethanone (21.9 mg, 0.089 mmol), palladium(II) acetate (1.5 mg, 0.007 mmol), triphenylphosphine (3.6 mg, 0.014 mmol), and tetra-*n*-butylammonium fluoride (1.0 M solution in tetrahydrofuran, 103 µl, 0.10 mmol). The reaction was stirred at 23 °C for 5 h. The suspension was then concentrated *in vacuo* and purified by column chromatography (gradient 20 – 50% ethyl acetate/hexane) to give compound **49** as yellow oil (46.0 mg, 0.058 mmol).

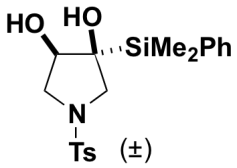
Yield 85%; IR (neat, cm^{-1}) 2970, 2935, 2869, 1681, 1632, 1611, 1589, 1515, 1467, 1393, 1365, 1341, 1270, 1157, 1081, 1036, 984, 954; HRMS (ESI-TOF) calcd. for $C_{44}H_{57}N_3O_{10}$ $[M+Na]^+$ 810.39362, found 810.39373; $[\alpha]_D^{22}$ = -65.1 (c = 3.4, $CHCl_3$).

I. Conversion of alkenyl silanes to α-silyl ketones

Dihydroxylation: to a solution of vinylsilane (1 equiv.) and 4-methylmorpholine 4-oxide (2 equiv.) in mixed solvent (acetone, water, and *tert*-butyl alcohol, 20:1:1, 0.1 M) was

added 0.7% of a 2.5% solution (w/v) of osmium tetroxide in *tert*-butyl alcohol. The reaction mixture was warmed up to 50 °C for 24 h and cooled to room temperature, and then aqueous $NaHSO_3$ (20%), was added. The resulting mixture was concentrated on the rotary evaporator (room temperature) to remove most of the *tert*-butyl alcohol and acetone, saturated with NaCl, and extracted five times with EA. The extract was then concentrated *in vacuo* and purified by column chromatography (gradient 50 – 100% ethyl acetate/hexane).

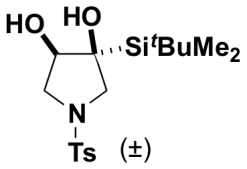
General procedure for silapinacol rearrangement: to a stirred solution of dihydroxylsilane (1 equiv.) in solvent (DCM, toluene or 1,4-dioxane, 25 mM) at 0 °C or r.t. was added the corresponding acid (1.2 equiv.). The resulting mixture was warmed up to the desired temperature and stirred for 16 hours. The reaction was then quenched with aqueous $NaHCO_3$ (saturated), extracted with EA, concentrated *in vacuo* and purified by column chromatography (gradient 20 – 50% ethyl acetate/hexane).



(3*R*,4*R*)-3-(dimethyl(phenyl)silyl)-1-tosylpyrrolidine-3,4-diol and its enantiomer(56)

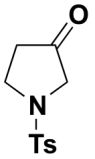
Yield 99% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2 H), 7.52-7.51 (m, 2 H), 7.44-7.36 (m, 3 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.05 (dd, *J* = 8.0, 15.5 Hz, 1 H), 3.46 (dd, *J* = 7.0, 14.5 Hz, 1 H), 3.40 (d, *J* = 12.5 Hz, 1 H), 3.33 (d, *J* = 12.5 Hz, 1 H), 3.02 (dd, *J* = 8.0, 9.5 Hz, 1 H), 2.42 (s, 3 H), 2.04 (d, *J* = 8.0 Hz, 1 H), 1.73 (s, 1 H), 0.39

(s, 3 H), 0.38 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.6, 134.3, 134.1, 133.6, 130.0, 129.7, 128.2, 127.4, 73.3, 72.2, 56.2, 51.2, 21.5, -5.9, -5.9.



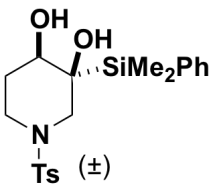
(3*R*,4*R*)-3-(*tert*-butyldimethylsilyl)-1-tosylpyrrolidine-3,4-diol and its enantiomer (57)

Yield 94% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2 H), 7.33 (d, *J* = 7.5 Hz, 2 H), 4.11(dd, *J* = 8.0, 16.0 Hz, 1 H), 3.50-3.44 (m, 2 H), 3.37 (d, *J* = 11.5 Hz, 1 H), 3.05 (dd, *J* = 7.5, 10.0 Hz, 1 H), 2.55 (d, *J* = 8.5 Hz, 1 H), 2.43 (s, 3 H), 1.88 (s, 1 H), 0.93 (s, 9 H), 0.03 (s, 3 H), -0.04 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.8, 133.6, 129.7, 127.5, 74.0, 73.4, 57.0, 51.1, 27.2, 21.5, 17.5, -7.5, -7.6.



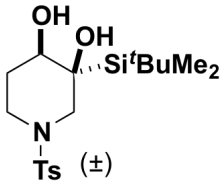
1-Tosylpyrrolidin-3-one (60)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 3.54 (d, *J* = 7.5 Hz, 2 H), 3.49 (s, 2 H), 2.50 (t, *J* = 7.5 Hz, 2 H), 2.45 (s, 3 H).



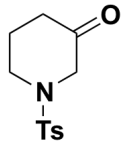
(3*R*,4*R*)-3-(dimethyl(phenyl)silyl)-1-tosylpiperidine-3,4-diol and its enantiomer (61)

Yield 82% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.58-7.54 (m, 4 H), 7.42-7.26 (m, 5 H), 3.53-3.51 (m, 1 H), 3.46-3.41 (m, 2 H), 2.46-2.43 (m, 4 H), 2.36-2.31 (m, 1 H), 2.14 (s, 1 H), 2.03 (d, *J* = 9.5 Hz, 1 H), 1.86-1.73 (m, 2 H), 0.46 (s, 3 H), 0.44 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.9, 135.2, 134.4, 132.9, 129.8, 129.7, 127.9, 127.6, 70.4, 66.6, 52.0, 44.2, 28.8, 21.5, -4.6, -5.1.



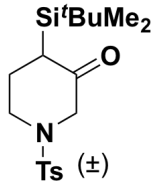
(3*R*,4*R*)-3-(*tert*-butyldimethylsilyl)-1-tosylpiperidine-3,4-diol and its enantiomer (62)

Yield 92% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2 H), 7.35-7.33 (m, 2 H), 3.80-3.77 (m, 1 H), 3.69-3.64 (m, 1 H), 3.53-3.48 (m, 1 H), 2.51 (d, *J* = 12.0 Hz, 1 H), 2.45 (s, 3 H), 2.20 (s, 1 H), 1.99 (d, *J* = 11.0 Hz, 1 H), 1.87-1.80 (m, 2 H), 0.95 (s, 9 H), 0.13-0.08 (m, 6 H).



1-Tosylpiperidin-3-one (65)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.0 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 3.60 (s, 2 H), 3.29 (t, *J* = 6.7 Hz, 2 H), 2.44 (s, 3 H), 2.36 (t, *J* = 6.7 Hz, 2 H), 2.04-1.99 (m, 2 H).



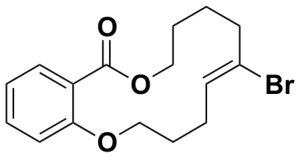
Racemic 4-(*tert*-butyldimethylsilyl)-1-tosylpiperidin-3-one (64)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 3.62 (d, *J* = 17.0 Hz, 2 H), 3.46-3.39 (m, 2 H), 2.99-2.94 (m, 2 H), 2.44-2.42 (m, 4 H), 2.22-2.06 (m, 2 H), 0.91 (s, 9 H), 0.11 (s, 3 H), 0.01 (s, 3 H).

J. Conversion of alkenylsiloxanes to alkenyl halides

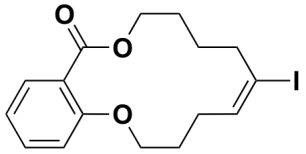
Dibromination/bromodesilylation: to a stirred solution of alkenylsiloxane (1 equiv.) in the corresponding solvent (50 mM) was added Br_2 (1.05 equiv.) at -78 °C. After 5 min at -78 °C, TBAF (1 M solution in THF, 4 equiv.) was added and the reaction was allowed to warm up to r.t. over 15 min and stirred at r.t. for another 15 min. The reaction was then quenched with aqueous $Na_2S_2O_3$ (10 %), extracted with EA. The extract was concentrated *in vacuo* and purified by column chromatography (gradient 0 – 10% ethyl acetate/hexane).

Iodination: adapted from reported procedure,[284] to a stirred solution of alkenylsiloxane (1 equiv.) in HFIP (50 mM) was added NIS (1.5 equiv.) at 0 °C. After 40 min at 0 °C, the reaction was then quenched with aqueous $Na_2S_2O_3$ (10 %), extracted with EA. The extract was concentrated *in vacuo* and purified by column chromatography (gradient 0 – 10% ethyl acetate/hexane).



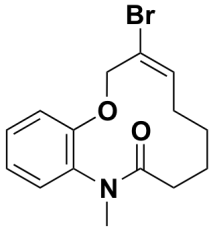
(*Z*)-6-bromo-3,4,7,8,9,10-hexahydrobenzo[*b*][1,5]dioxacyclotetradecin-12(2*H*)-one (66-*Z*)

Yield 89% (colorless oil); IR (neat, cm^{-1}) 2940, 1698, 1601, 1491, 1452, 1384, 1300, 1244, 11166, 1133, 1097, 1053; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1 H), 7.46-7.43 (m, 1 H), 7.00-6.94 (m, 1 H), 6.26 (t, *J* = 6.7 Hz, 1 H), 4.38 (t, *J* = 5.2 Hz, 2 H), 4.16 (t, *J* = 5.0 Hz, 2 H), 2.56-2.53 (m, 2 H), 2.44-2.40 (m, 2 H), 2.00-1.96 (m, 2 H), 1.89-1.84 (m, 2 H), 31.75-1.70 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.8, 157.6, 133.2, 132.1, 128.7, 125.6, 1206, 120.1, 112.1, 70.7, 65.0, 38.9, 31.7, 27.7, 25.6, 24.0.



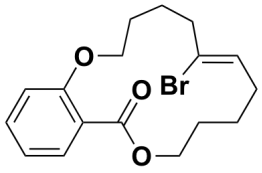
(*E*)-6-iodo-3,4,7,8,9,10-hexahydrobenzo[*b*][1,5]dioxacyclotetradecin-12(2*H*)-one (76-*E*)

Yield 93% (colorless oil); IR (neat, cm^{-1}) 2953, 1702, 1601, 1490, 1452, 1384, 1354, 1302, 1251, 1193, 1164, 1132, 1097, 1052, 979; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.77-7.75 (m, 1 H), 7.44-7.40 (m, 1 H), 6.99-6.92 (m, 2 H), 6.23 (t, *J* = 7.8 Hz, 1 H), 4.40 (t, *J* = 5.0 Hz, 2 H), 4.08 (t, *J* = 5.2 Hz, 2 H), 2.65-2.62 (m, 2 H), 2.27-2.23 (m, 2 H), 1.84-1.80 (m, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.3, 157.1, 140.1, 133.1, 132.2, 121.2, 120.2, 112.2, 101.6, 66.1, 63.7, 38.7, 28.9, 27.1, 26.6, 24.4.



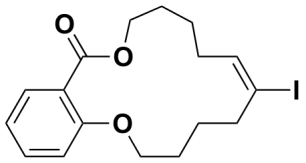
(*E*)-3-bromo-10-methyl-5,6,7,8-tetrahydro-2*H*-benzo[*b*][1,4]oxaazacyclododecin-9(10*H*)-one (71-*E*)

Yield 79% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.31 (m, 1 H), 7.18-7.16 (m, 1 H), 7.03-7.00 (m, 1 H), 6.93-6.92 (m, 1 H), 6.23-6.19 (m, 1 H), 4.96 (d, *J* = 12.5 Hz, 1 H), 4.73 (d, *J* = 13.0 Hz, 1 H), 3.20 (s, 3 H), 2.26-2.20 (m, 1 H), 2.01-1.84 (m, 4 H), 1.54-1.37 (m, 3 H).



(*Z*)-6-bromo-4,5,8,9,10,11-hexahydro-2*H*-benzo[*b*][1,5]dioxacyclopentadecin-13(3*H*)-one (74-*Z*)

Yield 97% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.69-7.67 (m, 1 H), 7.43-7.40 (m, 1 H), 7.00-6.97 (m, 2 H), 5.73 (t, *J* = 7.0 Hz, 1 H), 4.30 (t, *J* = 5.5 Hz, 2 H), 4.02 (t, *J* = 7.0 Hz, 2 H), 2.50 (t, *J* = 6.0 Hz, 2 H), 2.27-2.24 (m, 2 H), 1.91-1.85 (m, 2 H), 1.94-1.78 (m, 2 H), 1.74-1.69 (m, 2 H), 1.64-1.59 (m, 2 H).



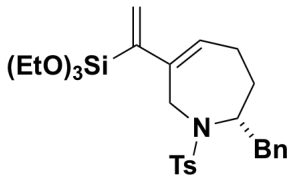
(*E*)-6-iodo-4,5,8,9,10,11-hexahydro-2*H*-benzo[*b*][1,5]dioxacyclopentadecin-13(3*H*)-one (77-*E*)

Yield 87% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.73-7.71 (m, 1 H), 7.43-7.40 (m, 1 H), 6.97 (dd, *J* = 8.0, 8.0 Hz, 1 H), 6.91 (d, *J* = 8.0 Hz, 1 H), 6.27 (t, *J* = 8.2 Hz, 1 H), 4.38 (t, *J* = 6.0 Hz, 2 H), 4.06 (t, *J* = 5.2 Hz, 2 H), 2.57 (t, *J* = 7.8 Hz, 2 H), 2.11-2.07 (m, 2 H), 1.92-1.86 (m, 2 H), 1.83-1.75 (m, 4 H), 1.60-1.54 (m, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 168.2, 157.5, 140.7, 132.9, 131.5, 121.2, 120.1, 112.3, 101.9, 67.8, 64.5, 39.4, 30.2, 27.9, 27.7, 26.3, 25.7.

K. Enyne RCM reactions

Alkyne silylation and enyne RCM (un-optimized conditions): to a stirred solution of 91 (100 mg, 0.27 mmol) in 2.7 mL THF (0.1 M) at -78 °C was added 0.14 mL butyllithium (2 M in hexane, 0.28 mmol) followed by chlorotriethoxysilane (108 mg, 0.54 mmol). The reaction was stirred for 1 hour at -78 °C and warmed up to room temperature. THF was removed on the rotary evaporator (room temperature). Without workup or purification, the crude reaction mixture was charged with anhydrous toluene (2.7 mL) and 51 mg (0.082 mmol) HG-II, purged with ethylene gas, and left at room temperature for overnight. The reaction was then quenched with aqueous $NaHCO_3$ (saturated), extracted with EA, concentrated *in vacuo* and purified by column chromatography (gradient 20 –

50% ethyl acetate/hexane) to give compound **92** as yellow oil (20 mg, 0.038 mmol, 20% yield).

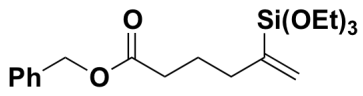


(*R*)-2-benzyl-1-tosyl-6-(1-(triethoxysilyl)vinyl)-2,3,4,7-tetrahydro-1*H*-azepine (92)

Yield 20% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.5 Hz, 2 H), 7.30-7.27 (m, 2 H), 7.24-7.17 (m, 5 H), 5.91-5.90 (m, 1 H), 5.78-5.78 (m, 1 H), 5.72-5.71 (m, 1 H), 4.63 (d, *J* = 18.5 Hz, 1 H), 4.01-3.95 (m, 1 H), 3.80 (q, *J* = 7.0 Hz, 7 H), 3.03 (dd, *J* = 13.0, 3.5 Hz, 1 H), 2.75 (dd, *J* = 13.0, 4.5 Hz, 1 H), 2.37 (s, 3 H), 2.03-1.96 (m, 1 H), 1.70-1.58 (m, 2 H), 1.45-1.39 (m, 1 H), 1.22 (t, *J* = 7.0 Hz, 9 H).

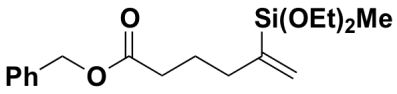
L. CM reactions

General reaction conditions for cross metathesis: to a stirred to solution of vinylsiloxane or alkenylsiloxane (1 equiv.) in toluene (0.1 M) was added the simple olefin (allyl acetate, methyl acrylate, or methylvinlylketone, 1 to 5 equiv.) and the catalyst (Cat. A, G-I, G-II, or HG-II, 20 mol%). The resulting mixture was warmed up to 50 °C and stirred for 16 hours. The crude reaction was then concentrated *in vacuo* and analyzed by ^{1}H NMR.



Benzyl 5-(triethoxysilyl)hex-5-enoate (94a)

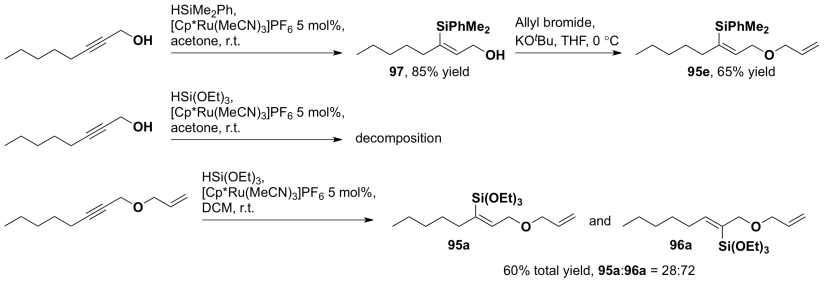
Yield 58% (colorless oil); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (m, 5 H), 5.72-5.71 (m, 1 H), 5.67-5.66 (m, 1 H), 5.12 (s, 2 H), 3.81 (q, *J* = 6.9 Hz, 6 H), 2.37 (t, *J* = 7.2 Hz, 2 H), 2.19 (t, *J* = 7.5 Hz, 2 H), 1.84 (tt, *J* = 6.9, 6.9 Hz, 2 H), 1.22 (t, *J* = 6.9 Hz, 9 H).



Benzyl 5-(diethoxy(methyl)silyl)hex-5-enoate (94c)

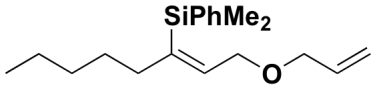
Yield 52% (colorless oil); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36-7.31 (m, 5 H), 5.68-5.66 (m, 1 H), 5.58-5.57 (m, 1 H), 5.12 (s, 2 H), 3.75 (q, *J* = 7.2 Hz, 4 H), 2.37 (t, *J* = 7.8 Hz, 2 H), 2.18 (t, *J* = 7.8 Hz, 2 H), 1.82 (tt, *J* = 7.8, 7.8 Hz, 2 H), 1.20 (t, *J* = 6.9 Hz, 6 H), 0.19 (s, 3 H).

Scheme I-22. Synthesis of **95e** and **95a**.



The synthesis of **95e** started from hydrosilylation of oct-2-yn-1-ol (Scheme **I-22**). Following the general hydrosilylation procedure with acetone as solvent instead of DCM, compound **97** was obtained with 85% yield. Allylation of **97** gave rise to compound **95e** with moderate yield. Surprisingly, hydrosilylation with $HSi(OEt)_3$ did not work. Instead, 1-(allyloxy)oct-2-yne was subjected to the hydrosilylation reaction. However, the reaction yielded the undesired regioisomer **96a** as the major product that is not separable

from the desired product **95a**. Cross metathesis reactions with **95e** or mixture of **95a** and **96a** were performed following the general procedure, but failed to generate any detectable amount of products.



(*Z*)-(1-(allyloxy)oct-2-en-3-yl)dimethyl(phenyl)silane (95e)

Yield 65% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.53-7.50 (m, 2 H), 7.36-7.32 (m, 3 H), 6.20 (t, *J* = 6.5 Hz, 1 H), 5.82-5.75 (m, 1 H), 5.18-5.14 (m, 1 H), 5.11-5.08 (m, 1 H), 3.82 (d, *J* = 7.0 Hz, 2 H), 3.74-3.73 (m, 2 H), 2.15 (t, *J* = 8.5 Hz, 2 H), 1.40-1.34 (m, 2 H), 1.31-1.23 (m, 4 H), 0.87 (t, *J* = 7.0 Hz, 3 H), 0.39 (s, 6 H).

References

(1) Nielsen, T. E.; Schreiber, S. L. *Angew. Chem.* **2008**, *47*, 48.

(2) Schreiber, S. L. *Science* **2000**, *287*, 1964.

(3) Comer, E.; Rohan, E.; Deng, L.; Porco, J. A., Jr. *Org. Lett.* **2007**, *9*, 2123.

(4) Burke, M. D.; Schreiber, S. L. *Angew. Chem.* **2004**, *43*, 46.

(5) Tietze, L. F.; Beifuss, U. *Angew. Chem. Int. Ed.* **1993**, *32*, 131.

(6) Luo, T.; Schreiber, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 5667.

(7) Peng, L. F.; Stanton, B. Z.; Maloof, N.; Wang, X.; Schreiber, S. L. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 6319.

(8) Marcaurelle, L. A.; Comer, E.; Dandapani, S.; Duvall, J. R.; Gerard, B.; Kesavan, S.; Lee, M. D.; Liu, H.; Lowe, J. T.; Marie, J.-C.; Mulrooney, C. A.; Pandya, B. A.; Rowley, A.; Ryba, T. D.; Suh, B.-C.; Wei, J.; Young, D. W.; Akella, L. B.; Ross, N. T.; Zhang, Y.-L.; Fass, D. M.; Reis, S. A.; Zhao, W.-N.; Haggarty, S. J.; Palmer, M.; Foley, M. A. *J. Am. Chem. Soc.* **2010**, *132*, 16962.

(9) Pizzirani, D.; Kaya, T.; Clemons, P. A.; Schreiber, S. L. *Org. Lett.* **2010**, *12*, 2822.

(10) Spiegel, D. A.; Schroeder, F. C.; Duvall, J. R.; Schreiber, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 14766.

(11) Kumagai, N.; Muncipinto, G.; Schreiber, S. L. *Angewandte Chemie* **2006**, *45*, 3635.

(12) Sello, J. K.; Andreana, P. R.; Lee, D.; Schreiber, S. L. *Org. Lett.* **2003**, *5*, 4125.

(13) Greco, M. N.; Maryanoff, B. E. *Adv. Amino Acid Mimetics Peptidomimetics* **1997**, *1*, 41.

(14) Asakawa, Y.; Toyota, M.; Tori, M.; Hashimoto, T. *Spectroscopy,* **2000**, *14*, 149.

(15) Berlinck, R. G. S. *Nat. Prod. Rep.* **2002**, *19*, 617.

(16) Claeson, P.; Claeson, U. P.; Tuchinda, P.; Reutrakul, V. *Stud. Nat. Prod. Chem.* **2002**, *26*, 881.

(17) Ishibashi, M. In *Macrolide antibiotics*; Academic Press: **2002**, 57.

(18) Kohli, R. M.; Walsh, C. T. *Chem. Commun.* **2003**, 297.

(19) Walsh, C. T.; O'Connor, S. E.; Schneider, T. L. *J. Ind. Microbiol. Biotechnol.* **2003**, *30*, 448.

(20) Walsh, C. T. *Science* **2004**, *303*, 1805.

(21) Simmons, T. L.; Andrianasolo, E.; McPhail, K.; Flatt, P.; Gerwick, W. H. *Mol. Cancer Ther.* **2005**, *4*, 333.

(22) Wessjohann, L. A.; Ruijter, E.; Garcia-Rivera, D.; Brandt, W. *Mol. Diversity* **2005**, *9*, 171.

(23) Gruenewald, J.; Marahiel, M. A. In *Handbook of Biologically Active Peptides*; Elsevier Inc.: **2006**, 89.

(24) Khosla, C.; Tang, Y.; Chen, A. Y.; Schnarr, N. A.; Cane, D. E. *Annu. Rev. Biochem.* **2007**, *76*, 195.

(25) Kopp, F.; Marahiel, M. A. *Nat. Prod. Rep.* **2007**, *24*, 735.

(26) Asakawa, Y.; Toyota, M.; Hashimoto, T.; Tori, M.; Nagashima, F.; Harinantenaina, L. *Heterocycles* **2008**, *76*, 99.

(27) Lachia, M.; Moody, C. J. *Nat. Prod. Rep.* **2008**, *25*, 227.

(28) Walsh, C. T. *Acc. Chem. Res.* **2008**, *41*, 4.

(29) Buchholz, T. J.; Kittendorf, J. D.; Sherman, D. H. In *Wiley Encyclopedia of Chemical Biology*; John Wiley & Sons, Inc.: **2009**, *3*, 746.

(30) Napolitano, J. G.; Daranas, A. H.; Norte, M.; Fernandez, J. J. *Anti-Cancer Agents Med. Chem.* **2009**, *9*, 122.

(31) Li, Y.; Pattenden, G. *Nat. Prod. Rep.* **2011**, *28*, 1269.

(32) Li, Y.; Pattenden, G. *Nat. Prod. Rep.* **2011**, *28*, 429.

(33) Mohd Nor, S. M.; Xu, Z.; Ye, T. In *Heterocycles in Natural Product Synthesis*; Wiley-VCH Verlag GmbH & Co. KGaA: 2011, p 569.

(34) McGuire, J. M.; Bunch, R. L.; Anderson, R. C.; Boaz, H. E.; Flynn, E. H.; Powell, H. M.; Smith, J. W. *Schweiz. Med. Wochenschr.* **1952**, *82*, 1064.

(35) Sensi, P.; Margalith, P.; Timbal, M. T. *Farmaco. Sci.* **1959**, *14*, 146.

(36) Brufani, M.; Fedeli, W.; Giacomello, G.; Vaciago, A. *Experientia* **1964**, *20*, 339.

(37) Schwartz, B. S.; Warren, M. R.; Barkley, F. A.; Landis, L. *Antibiot. Annu.* **1959**, *7*, 41.

(38) Wright, W. W.; Welch, H. *Antibiot. Annu.* **1959**, *7*, 61.

(39) Ehlert, F.; Neu, H. C. *Eur. J. Clin. Microbiol.* **1987**, *6*, 84.

(40) Griffith, R. S.; Peck, F. B., Jr. *Antibiot. Annu.* **1955**, *3*, 619.

(41) McGuire, J. M.; Wolfe, R. N.; Ziegler, D. W. *Antibiot. Annu.* **1955**, *3*, 612.

(42) McCormick, M. H.; McGuire, J. M.; Pittenger, G. E.; Pittenger, R. C.; Stark, W. M. *Antibiot. Annu.* **1955**, *3*, 606.

(43) Oura, M.; Sternberg, T. H.; Wright, E. T. *Antibiot. Annu.* **1955**, *3*, 566.

(44) Sehgal, S. N.; Baker, H.; Vezina, C. *J. Antibiot. (Tokyo)* **1975**, *28*, 727.

(45) Vezina, C.; Kudelski, A.; Sehgal, S. N. *J. Antibiot. (Tokyo)* **1975**, *28*, 721.

(46) Ruegger, A.; Kuhn, M.; Lichti, H.; Loosli, H. R.; Huguenin, R.; Quiquerez, C.; von Wartburg, A. *Helv. Chim. Acta.* **1976**, *59*, 1075.

(47) Calne, R. Y.; White, D. J.; Thiru, S.; Evans, D. B.; McMaster, P.; Dunn, D. C.; Craddock, G. N.; Pentlow, B. D.; Rolles, K. *Lancet* **1978**, *2*, 1323.

(48) Hofle, G. H.; Bedorf, N.; Steinmetz, H.; Schomburg, D.; Gerth, K.; Reichenbach, H. *Angew. Chem. In. Ed. Engl.* **1996**, *35*, 1567.

(49) Campistol, J. M.; Gutierrez-Dalmau, A.; Torregrosa, J. V. *Transplantation* **2004**, *77*, 760.

(50) Chan, S. *Br. J. Cancer* **2004**, *91*, 1420.

(51) Wendel, H.-G.; Stanchina, E. d.; Fridman, J. S.; Malina, A.; Ray, S.; Kogan, S.; Cordon-Cardo, C.; Pelletier, J.; Lowe, S. W. *Nature* **2004**, *428*, 332.

(52) Kumar, N.; Kiuchi, M.; Tallarico, J. A.; Schreiber, S. L. *Org. Lett.* **2005**, *7*, 2535.

(53) Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. P. *Chem. Rev.* **2009**, *109*, 2551.

(54) Parenty, A.; Moreau, X.; Campagne, J. M. *Chem. Rev.* **2006**, *106*, 911.

(55) Shiina, I.; Katoh, T.; Nagai, S.; Hashizume, M. *Chem. Rec.* **2009**, *9*, 305.

(56) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. In *Handbook of Cyclization Reactions*; Wiley-VCH Verlag GmbH & Co. KGaA: **2010**, *2*, 1055.

(57) Marco, J. A.; Carda, M. *Nat. Prod. Commun.* **2011**, *6*, 505.

(58) Bai, D.; Bo, Y. *Youji Huaxue* **1991**, *11*, 132.

(59) Li, P.; Roller, P. P.; Xu, J. *Curr. Org. Chem.* **2002**, *6*, 411.

(60) Davies, J. S. *J. Pept. Sci.* **2003**, *9*, 471.

(61) Boddy, C. N. *Chem. Biol.* **2004**, *11*, 1599.

(62) Lu, Z.-k.; Xian, Y.-f.; Li, D.-f. *Huaxue Gongchengshi* **2006**, *20*, 43.

(63) Jiang, S.; Li, Z.; Ding, K.; Roller, P. P. *Curr. Org. Chem.* **2008**, *12*, 1502.

(64) Gokel, G. W.; Durst, H. D. *Synthesis* **1976**, 168.

(65) Atkins, T. J.; Richman, J. E.; Oettle, W. F. *Org. Synth.* **1978**, *58*, 86.

(66) Buter, J.; Kellogg, R. M. *Org. Synth.* **1987**, *65*, 150.

(67) Galli, C.; Mandolini, L. *Org. Synth.* **1978**, *58*, 98.

(68) Gokel, G. W.; Cram, D. J.; Liotta, C. L.; Harris, H. P.; Cook, F. L. *Org. Synth.* **1977**, *57*, 30.

(69) Kan, T.; Fukuyama, T. *Chem. Commun.* **2004**, 353.

(70) Pedersen, C. J. *Org. Synth.* **1972**, *52*, 66.

(71) Zhu, J. *Synlett* **1997**, 133.

(72) Zhu, J. *Methods Mol. Med.* **1999**, *23*, 293.

(73) Herzner, H.; Ruck-Braun, K. In *Organic Synthesis Highlights IV*; Wiley-VCH Verlag GmbH: **2000**, 281.

(74) Wang, Q.; Zhu, J. *Chimia* **2011**, *65*, 168.

(75) Nakada, M. *Yakugaku Zasshi* **1997**, *117*, 486.

(76) Prunet, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 2826.

(77) Gaich, T.; Weinstabl, H.; Mulzer, J. *Synlett* **2009**, 1357.

(78) Halweg, K. M.; Gladysz, J. A. *Strem Chem.* **1981**, *9*, 7.

(79) Sonogashira, K. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; John Wiley & Sons, Inc.: **2002**, *1*, 493.

(80) Moreno-Manas, M.; Pleixats, R.; Sebastian, R. M.; Vallribera, A.; Roglans, A. *J. Organomet. Chem.* **2004**, *689*, 3669.

(81) Lukashev, N. V.; Averin, A. D.; Latyshev, G. V.; Donez, P. A.; Ranyuk, E. R.; Beletskaya, I. P. *Pol. J. Chem.* **2006**, *80*, 559.

(82) Majumdar, K. C.; Chattopadhyay, B. *Curr. Org. Chem.* **2009**, *13*, 731.

(83) Averin, A. D.; Uglov, A. N.; Lemeune, A.; Guilard, R.; Beletskaya, I. P. In *Heterocyclic Compounds*; Nova Science Publishers, Inc.: **2010**, 119.

(84) Beletskaya, I. P.; Averin, A. D.; Bessmertnykh, A. G.; Denat, F.; Guilard, R. *Russ. J. Org. Chem.* **2010**, *46*, 947.

(85) Patil, N. T.; Yamamoto, Y. In *Handbook of Cyclization Reactions*; Wiley-VCH Verlag GmbH & Co. KGaA: **2010**, *1*, 457.

(86) Evano, G.; Toumi, M.; Coste, A. *Chem. Commun.* **2009**, 4166.

(87) Stefani, H. A.; Guarezemini, A. S.; Cella, R. *Tetrahedron* **2010**, *66*, 7871.

(88) Iyoda, M. *Adv. Synth. Catal.* **2009**, *351*, 984.

(89) Wessjohann, L. A.; Scheid, G. *Synthesis* **1999**, 1.

(90) Dong, C.-G.; Henderson, J. A.; Kaburagi, Y.; Sasaki, T.; Kim, D.-S.; Kim, J. T.; Urabe, D.; Guo, H.; Kishi, Y. *J. Am. Chem. Soc.* **2009**, *131*, 15642.

(91) Nolan, S. P.; Clavier, H. *Chem. Soc. Rev.* **2010**, *39*, 3305.

(92) Prunet, J. *Eur. J. Org. Chem.* **2011**, *2011*, 3634.

(93) Brenneman, J. B.; Martin, S. F. *Curr. Org. Chem.* **2005**, *9*, 1535.

(94) Fuerstner, A. *Eur. J. Org. Chem.* **2004**, 943.

(95) Mulzer, J.; Oehler, E. *Top. Organomet. Chem.* **2004**, *13*, 269.

(96) Furstner, A. *Angew. Chem. Int. Ed.***2000**, *39*, 3012.

(97) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem. Int. Ed.***2005**, *44*, 4490.

(98) Deiters, A.; Martin, S. F. *Chemical Reviews* **2004**, *104*, 2199.

(99) Furstner, A. *Top. Catal.* **1997**, *4*, 285.

(100) Gaich, T.; Mulzer, J. *Curr. Top. Med. Chem.* **2005**, *5*, 1473.

(101) Martin, W. H. C.; Blechert, S. *Curr. Top. Med. Chem.* **2005**, *5*, 1521.

(102) Conrad, J. C.; Fogg, D. E. *Curr. Org. Chem.* **2006**, *10*, 185.

(103) Majumdar, K. C.; Rahaman, H.; Roy, B. *Curr. Org. Chem.* **2007**, *11*, 1339.

(104) de Weghe, P. V.; Eustache, J. *Curr. Top. Med. Chem.* **2005**, *5*, 1495.

(105) Rouge, d. S. A.; Kaiser, C. R.; Ferezou, J.-P. *Quim. Nova* **2008**, *31*, 655.

(106) Gradillas, A.; Perez-Castells, J. *Angew. Chem. Int. Ed.***2006**, *45*, 6086.

(107) Arisawa, M.; Nishida, A.; Nakagawa, M. *J. Organomet. Chem.* **2006**, *691*, 5109.

(108) Martin, S. F. *Pure. Appl. Chem.* **2005**, *77*, 1207.

(109) Maier, M. E. *Angew. Chem. Int. Ed.***2000**, *39*, 2073.

(110) Nicolaou, K. C.; King, N. P.; He, Y. *Top. Organomet. Chem.* **1998**, *1*, 73.

(111) Chattopadhyay, S. K.; Karmakar, S.; Biswas, T.; Majumdar, K. C.; Rahaman, H.; Roy, B. *Tetrahedron* **2007**, *63*, 3919.

(112) Rivkin, A.; Cho, Y. S.; Gabarda, A. E.; Yoshimura, F.; Danishefsky, S. J. *J. Nat. Prod.* **2004**, *67*, 139.

(113) Gradillas, A.; Perez-Castells, J. In *Metathesis in Natural Product Synthesis*; Wiley-VCH Verlag GmbH & Co. KGaA: **2010**, 149.

(114) Hassan, H. M. A. *Chem. Commun.* **2010**, *46*, 9100.

(115) Morzycki, J. W. *Steroids* **2011**, *76*, 949.

(116) Prunet, J.; Rouge, d. S. A.; Ferezou, J.-P. In *Modern Supramolecular Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: **2008**, 29.

(117) Davies, P. W. In *Metathesis in Natural Product Synthesis;* Wiley-VCH Verlag GmbH & Co. KGaA: **2010**, 205.

(118) Looper, R. E.; Pizzirani, D.; Schreiber, S. L. *Org. Lett.* **2006**, *8*, 2063.

(119) Molteni, G.; Zecchi, G. *Trends Heterocycl. Chem.* **1997**, *5*, 127.

(120) Dedola, S.; Nepogodiev, S. A.; Field, R. A. *Org. Biomol. Chem.* **2007**, *5*, 1006.

(121) Dondoni, A. *Asian J. Chem.* **2007**, *2*, 700.

(122) Tron, G. C.; Pirali, T.; Billington, R. A.; Canonico, P. L.; Sorba, G.; Genazzani, A. A. *Med. Res. Rev.* **2008**, *28*, 278.

(123) Fraunhoffer, K. J.; Prabagaran, N.; Sirois, L. E.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 9032.

(124) Stang, E. M.; Christina, W. M. *Nat. Chem.* **2009**, *1*, 547.

(125) Crane, E. A.; Scheidt, K. A. *Angew. Chem. Int. Ed.* **2010**, *49*, 8316.

(126) Wessjohann, L. A.; Ruijter, E. *Mol. Diversity* **2005**, *9*, 159.

(127) Wessjohann, L. A.; Rivera, D. G.; Vercillo, O. E. *Chem. Rev. (Washington, DC, U. S.)* **2009**, *109*, 796.

(128) Masson, G.; Neuville, L.; Bughin, C.; Fayol, A.; Zhu, J. *Top. Heterocycl. Chem.* **2010**, *25*, 1.

(129) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

(130) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(131) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100.

(132) Madsen, C. M.; Clausen, M. H. *Eur. J. Org. Chem.* **2011**, 3107.

(133) Moretto, A.; Crisma, M.; Formaggio, F.; Toniolo, C. *Biopolymers* **2010**, *94*, 721.

(134) Chase, P. A.; Lutz, M.; Spek, A. L.; van, K. G. P. M.; van, K. G. *J. Mol. Catal. A: Chem.* **2006**, *254*, 2.

(135) Dupouy, C.; Payrastre, C.; Escudier, J.-M. *Targets Heterocycl. Syst.* **2008**, *12*, 185.

(136) Ibrahim, Y. A. *J. Mol. Catal. A: Chem.* **2006**, *254*, 43.

(137) Blom, P.; Ruttens, B.; Van, H. S.; Hubrecht, I.; Van, d. E. J.; Sas, B.; Van, h. J.; Vandenkerckhove, J. *J. Org. Chem.* **2005**, *70*, 10109.

(138) Ruttens, B.; Blom, P.; Van, H. S.; Hubrecht, I.; Van, d. E. J.; Sas, B.; Van, H. J.; Vandenkerckhove, J. *J. Org. Chem.* **2007**, *72*, 5514.

(139) Coghlan, D. R.; Bremner, J. B.; Keller, P. A.; Pyne, S. G.; David, D. M.; Somphol, K.; Baylis, D.; Coates, J.; Deadman, J.; Rhodes, D. I.; Robertson, A. D. *Bioorg. Med. Chem.* **2011**, *19*, 3549.

(140) Perez-Balado, C.; Nebbioso, A.; Rodriguez-Grana, P.; Minichiello, A.; Miceli, M.; Altucci, L.; de, L. A. R. *J. Med. Chem.* **2007**, *50*, 2497.

(141) Terracciano, S.; Chini, M. G.; Bifulco, G.; D'Amico, E.; Marzocco, S.; Riccio, R.; Bruno, I. *Tetrahedron* **2010**, *66*, 2520.

(142) Goudreau, N.; Brochu, C.; Cameron, D. R.; Duceppe, J.-S.; Faucher, A.-M.; Ferland, J.-M.; Grand-Maitre, C.; Poirier, M.; Simoneau, B.; Tsantrizos, Y. S. *J. Org. Chem.* **2004**, *69*, 6185.

(143) Oishi, S.; Shi, Z.-D.; Worthy, K. M.; Bindu, L. K.; Fisher, R. J.; Burke, T. R. *Chembiochem* **2005**, *6*, 668.

(144) Ersmark, K.; Nervall, M.; Gutierrez-de-Teran, H.; Hamelink, E.; Janka, L. K.; Clemente, J. C.; Dunn, B. M.; Gogoll, A.; Samuelsson, B.; Aaqvist, J.; Hallberg, A. *Bioorg. Med. Chem.* **2006**, *14*, 2197.

(145) Tsantrizos, Y. S.; Ferland, J.-M.; McClory, A.; Poirier, M.; Farina, V.; Yee, N. K.; Wang, X.-j.; Haddad, N.; Wei, X.; Xu, J.; Zhang, L. *J. Organomet. Chem.* **2006**, *691*, 5163.

(146) Tao, Z.-F.; Wang, L.; Stewart, K. D.; Chen, Z.; Gu, W.; Bui, M.-H.; Merta, P.; Zhang, H.; Kovar, P.; Johnson, E.; Park, C.; Judge, R.; Rosenberg, S.; Sowin, T.; Lin, N.-H. *J. Med. Chem.* **2007**, *50*, 1514.

(147) Abell, A. D.; Jones, M. A.; Coxon, J. M.; Morton, J. D.; Aitken, S. G.; McNabb, S. B.; Lee, H. Y. Y.; Mehrtens, J. M.; Alexander, N. A.; Stuart, B. G.; Neffe, A. T.; Bickerstaffe, R. *Angew. Chem. Int. Ed.* **2009**, *48*, 1455.

(148) Huber, T.; Manzenrieder, F.; Kuttruff, C. A.; Dorner-Ciossek, C.; Kessler, H. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 4427.

(149) Velazquez, F.; Venkatraman, S.; Blackman, M.; Pinto, P.; Bogen, S.; Sannigrahi, M.; Chen, K.; Pichardo, J.; Hart, A.; Tong, X.; Girijavallabhan, V.; Njoroge, F. G. *J. Med. Chem.* **2009**, *52*, 700.

(150) Lampa, A.; Ehrenberg, A. E.; Vema, A.; Aakerblom, E.; Lindeberg, G.; Danielson, U. H.; Karlen, A.; Sandstroem, A. *Bioorg. Med. Chem.* **2011**, *19*, 4917.

(151) Lee, D.; Sello, J. K.; Schreiber, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 10648.

(152) Kim, Y.-k.; Arai, M. A.; Arai, T.; Lamenzo, J. O.; Dean, E. F., III; Patterson, N.; Clemons, P. A.; Schreiber, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 14740.

(153) Stanton, B. Z.; Peng, L. F.; Maloof, N.; Nakai, K.; Wang, X.; Duffner, J. L.; Taveras, K. M.; Hyman, J. M.; Lee, S. W.; Koehler, A. N.; Chen, J. K.; Fox, J. L.; Mandinova, A.; Schreiber, S. L. *Nat. Chem. Biol.* **2009**, *5*, 154.

(154) Meng, D.; Bertinato, P.; Balog, A.; Su, D.-S.; Kamenecka, T.; Sorensen, E. J.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 10073.

(155) Nicolaou, K. C.; He, Y.; Vourloumis, D.; Vallberg, H.; Roschangar, F.; Sarabia, F.; Ninkovic, S.; Yang, Z.; Trujillo, J. I. *J. Am. Chem. Soc.* **1997**, *119*, 7960.

(156) Yang, Z.; He, Y.; Vourloumis, D.; Vallberg, H.; Nicolaou, K. C. *Angew. Chem. Int. Ed.* **1997**, *36*, 166.

(157) Schinzer, D.; Bauer, A.; Bohm, O. M.; Limberg, A.; Cordes, M. *Chem. --Eur. J.* **1999**, *5*, 2483.

(158) Young, I. S.; Kerr, M. A. *J. Am. Chem. Soc.* **2007**, *129*, 1465.

(159) Jakubec, P.; Cockfield, D. M.; Dixon, D. J. *J. Am. Chem. Soc.* **2009**, *131*, 16632.

(160) Reddy, C. R.; Dharmapuri, G.; Rao, N. N. *Org. Lett.* **2009**, *11*, 5730.

(161) Llàcer, E.; Urpí, F.; Vilarrasa, J. *Org. Lett.* **2009**, *11*, 3198.

(162) Diaz-Oltra, S.; Angulo-Pachon, C. A.; Murga, J.; Carda, M.; Marco, J. A. *J. Org. Chem.* **2010**, *75*, 1775.

(163) Fuerstner, A.; Stelzer, F.; Rumbo, A.; Krause, H. *Chem.--Eur. J.* **2002**, *8*, 1856.

(164) Furstner, A.; Radkowski, K. *Chem Commun* **2002**, 2182.

(165) Lacombe, F.; Radkowski, K.; Seidel, G.; Fürstner, A. *Tetrahedron* **2004**, *60*, 7315.

(166) Furstner, A.; Guth, O.; Rumbo, A.; Seidel, G. *J. Am. Chem. Soc.* **1999**, *121*, 11108.

(167) Furstner, A.; Stelzer, F.; Rumbo, A.; Krause, H. *Chem-Eur J* **2002**, *8*, 1856.

(168) Bunz, U. H. F.; Kloppenburg, L. *Angew. Chem. Int. Ed.***1999**, *38*, 478.

(169) Furstner, A.; Davies, P. W. *Chem Commun* **2005**, 2307.

(170) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962.

(171) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 693.

(172) Meek, S. J.; O'Brien, R. V.; Llaveria, J.; Schrock, R. R.; Hoveyda, A. H. *Nature (London, U. K.)* **2011**, *471*, 461.

(173) Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature (London, U. K.)* **2011**, *479*, 88.

(174) Vougioukalakis, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 2234.

(175) Tsuboi, K.; Nakamura, T.; Suzuki, T.; Nakazaki, A.; Kobayashi, S. *Tetrahedron Lett.* **2010**, *51*, 1876.

(176) Pansare, S. V.; Adsool, V. A. *Org. Lett.* **2006**, *8*, 5897.

(177) Miles, J. A. L.; Mitchell, L.; Percy, J. M.; Singh, K.; Uneyama, E. *J. Org. Chem.* **2007**, *72*, 1575.

(178) Fellows, I. M.; Kaelin, D. E.; Martin, S. F. *J. Am. Chem. Soc.* **2000**, *122*, 10781.

(179) Hanessian, S.; Guesne, S.; Chenard, E. *Org. Lett.* **2010**, *12*, 1816.

(180) Yadav, J. S.; Satheesh, G.; Murthy, C. V. S. R. *Org. Lett.* **2010**, *12*, 2544.

(181) Bujard, M.; Briot, A.; Gouverneur, V.; Mioskowski, C. *Tetrahedron Lett.* **1999**, *40*, 8785.

(182) Burgey, C. S.; Paone, D. V.; Shaw, A. W.; Deng, J. Z.; Nguyen, D. N.; Potteiger, C. M.; Graham, S. L.; Vacca, J. P.; Williams, T. M. *Org. Lett.* **2008**, *10*, 3235.

(183) Li, S.-R.; Chen, P.-Y.; Chen, L.-Y.; Lo, Y.-F.; Tsai, I.-L.; Wang, E.-C. *Tetrahedron Lett.* **2009**, *50*, 2121.

(184) Le, B. B.; Goodman, A. J.; Michaut, M.; Ye, H.-F.; Graczyk, T. M.; Belanger, S.; Herbertz, T.; Yap, G. P. A.; DeHaven, R. N.; Dolle, R. E. *J. Med. Chem.* **2006**, *49*, 7278.

(185) Briggs, T. F.; Dudley, G. B. *Tetrahedron Lett.* **2005**, *46*, 7793.

(186) Cho, C.-G.; Kim, W.-S.; Smith, A. B., III *Org. Lett.* **2005**, *7*, 3569.

(187) Deiters, A.; Pettersson, M.; Martin, S. F. *J. Org. Chem.* **2006**, *71*, 6547.

(187) Kim, J. M.; Lee, K. Y.; Lee, S.; Kim, J. N. *Tetrahedron Lett.* **2004**, *45*, 2805.

(189) Liu, Q.; Jia, Y. *Org. Lett.* **2011**, *13*, 4810.

(190) Matsuya, Y.; Yamakawa, Y.-I.; Tohda, C.; Teshigawara, K.; Yamada, M.; Nemoto, H. *Org. Lett.* **2009**, *11*, 3970.

(191) Schwaeblein, A.; Martens, J. *Eur. J. Org. Chem.* **2011**, *2011*, 4335.

(192) Toueg, J.; Prunet, J. *Synlett* **2006**, 2807.

(193) Yoshida, K.; Kawagoe, F.; Hayashi, K.; Horiuchi, S.; Imamoto, T.; Yanagisawa, A. *Org. Lett.* **2009**, *11*, 515.

(194) Matsuda, T.; Yamaguchi, Y.; Ishida, N.; Murakami, M. *Synlett* **2010**, 2743.

(195) Xie, Q.; Denton, R. W.; Parker, K. A. *Org. Lett.* **2008**, *10*, 5345.

(196) Schuman, M.; Gouverneur, V. *Tetrahedron Lett.* **2002**, *43*, 3513.

(197) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17644.

(198) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726.

(199) Teng, X.; Cefalo, D. R.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 10779.

(200) Renaud, J.; Ouellet, S. G. *J. Am. Chem. Soc.* **1998**, *120*, 7995.

(201) Jang, H.; Zhugralin, A. R.; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 7859.

(202) Hekking, K. F. W.; Van, D. F. L.; Rutjes, F. P. J. T. *Tetrahedron* **2003**, *59*, 6751.

(203) Okada, A.; Ohshima, T.; Shibasaki, M. *Tetrahedron Lett.* **2001**, *42*, 8023.

(204) Rainier, J. D.; Cox, J. M.; Allwein, S. P. *Tetrahedron Lett.* **2001**, *42*, 179.

(205) Ceccon, J.; Danoun, G.; Greene, A. E.; Poisson, J.-F. *Org. Biomol. Chem.* **2009**, *7*, 2029.

(206) Grotenbreg, G. M.; Tuin, A. W.; Witte, M. D.; Leeuwenburgh, M. A.; Van, B. J. H.; Van, d. M. G. A.; Overkleeft, H. S.; Overhand, M. *Synlett* **2004**, 904.

(207) Risseeuw, M. D. P.; Grotenbreg, G. M.; Witte, M. D.; Tuin, A. W.; Leeuwenburgh, M. A.; Van, d. M. G. A.; Overkleeft, H. S.; Overhand, M. *Eur. J. Org. Chem.* **2006**, 3877.

(208) Salim, S. S.; Bellingham, R. K.; Satcharoen, V.; Brown, R. C. D. *Org. Lett.* **2003**, *5*, 3403.

(209) Marhold, M.; Buer, A.; Hiemstra, H.; van Maarseveen, J. H.; Haufe, G. *Tetrahedron Lett.* **2004**, *45*, 57.

(210) Chao, W.; Meketa, M. L.; Weinreb, S. M. *Synthesis* **2004**, 2058.

(211) Chao, W.; Weinreb, S. M. *Org. Lett.* **2003**, *5*, 2505.

(212) Paone, D. V.; Shaw, A. W.; Nguyen, D. N.; Burgey, C. S.; Deng, J. Z.; Kane, S. A.; Koblan, K. S.; Salvatore, C. A.; Mosser, S. D.; Johnston, V. K.; Wong, B. K.; Miller-Stein, C. M.; Hershey, J. C.; Graham, S. L.; Vacca, J. P.; Williams, T. M. *J. Med. Chem.* **2007**, *50*, 5564.

(213) Polito, L.; Cravini, M.; Poletti, L.; Lay, L. *Synth. Commun.* **2006**, *36*, 2203.

(214) Lebrun, S.; Couture, A.; Deniau, E.; Grandclaudon, P. *Tetrahedron Lett.* **2011**, *52*, 1481.

(215) Kasaya, Y.; Hoshi, K.; Terada, Y.; Nishida, A.; Shuto, S.; Arisawa, M. *Eur. J. Org. Chem.* **2009**, 4606.

(216) Dunne, K. S.; Bisaro, F.; Odell, B.; Paris, J.-M.; Gouverneur, V. *J. Org. Chem.* **2005**, *70*, 10803.

(217) Furstner, A.; Thiel, O. R.; Ackermann, L. *Org. Lett.* **2001**, *3*, 449.

(218) MacNaughtan, M. L.; Johnson, M. J. A.; Kampf, J. W. *J. Am. Chem. Soc.* **2007**, *129*, 7708.

(219) Berris, B. C.; Vollhardt, K. P. C. *Tetrahedron* **1982**, *38*, 2911.

(220) Brenneman, J. B.; Machauer, R.; Martin, S. F. *Tetrahedron* **2004**, *60*, 7301.

(221) Grimm, J. B.; Lee, D. *J. Org. Chem.* **2004**, *69*, 8967.

(222) Grimm, J. B.; Otte, R. D.; Lee, D. *J. Organomet. Chem.* **2005**, *690*, 5508.

(223) Kim, Y. J.; Grimm, J. B.; Lee, D. *Tetrahedron Lett.* **2007**, *48*, 7961.

(224) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020.

(225) Mori, M.; Wakamatsu, H.; Sato, Y.; Fujita, R. *J. Mol. Catal. A: Chem.* **2006**, *254*, 64.

(226) Park, S.; Kim, M.; Lee, D. *J. Am. Chem. Soc.* **2005**, *127*, 9410.

(227) Gallenkamp, D.; Furstner, A. *J. Am. Chem. Soc.* **2011**, *133*, 9232.

(228) Pietraszuk, C.; Fischer, H. *Chem. Commun.* **2000**, 2463.

(229) Pietraszuk, C.; Marciniec, B.; Fischer, H. *Organometallics* **2000**, *19*, 913.

(230) Pietraszuk, C.; Fischer, H. *Organometallics* **2001**, *20*, 4641.

(231) Kujawa-Welten, M.; Marciniec, B. *J. Mol. Catal. A: Chem.* **2002**, *190*, 79.

(232) Kujawa-Welten, M.; Pietraszuk, C.; Marciniec, B. *Organometallics* **2002**, *21*, 840.

(233) Pietraszuk, C.; Marciniec, B.; Fischer, H. *Tetrahedron Lett.* **2003**, *44*, 7121.

(234) Pietraszuk, C.; Fischer, H.; Rogalski, S.; Marciniec, B. *J. Organomet. Chem.* **2005**, *690*, 5912.

(235) Zak, P.; Pietraszuk, C.; Marciniec, B. *J. Mol. Catal. A: Chem.* **2008**, *289*, 1.

(236) Stewart, I. C.; Ung, T.; Pletnev, A. A.; Berlin, J. M.; Grubbs, R. H.; Schrodi, Y. *Org. Lett.* **2007**, *9*, 1589.

(237) Hong, S. H.; Chlenov, A.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5148.

(238) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746.

(239) Chatterjee, A. K.; Choi, T. L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360.

(240) Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981.

(241) Monfette, S.; Fogg, D. E. *Chem. Rev.* **2009**, *109*, 3783.

(242) Furstner, A.; Langemann, K. *J. Org. Chem.* **1996**, *61*, 3942.

(243) Lee, C. W.; Grubbs, R. H. *J. Org. Chem.* **2001**, *66*, 7155.

(244) Tamao, K.; Kumada, M.; Maeda, K. *Tetrahedron Lett.* **1984**, *25*, 321.

(245) Jin, J.; Chen, Y. L.; Li, Y. N.; Wu, J. L.; Dai, W. M. *Org. Lett.* **2007**, *9*, 2585.

(246) Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.* **1989**, *30*, 6051.

(247) Oi, S.; Taira, A.; Honma, Y.; Inoue, Y. *Org. Lett.* **2003**, *5*, 97.

(248) Sanada, T.; Kato, T.; Mitani, M.; Mori, A. *Adv. Synth. Catal.* **2006**, *348*, 51.

(249) Davis, A. P.; Hughes, G. J.; Lowndes, P. R.; Robbins, C. M.; Thomas, E. J.; Whitham, G. H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1934.

(250) Inoue, T.; Sato, T.; Kuwajima, I. *J. Org. Chem.* **1984**, *49*, 4671.

(251) Matsuda, I.; Sato, S.; Hattori, M.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 3215.

(252) Sato, S.; Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 1527.

(253) Matsuda, I.; Sato, S. *J. Organomet. Chem.* **1986**, *314*, 47.

(254) Enders, D.; Lohray, B. B. *Angew. Chem.* **1988**, *100*, 594.

(255) Larson, G. L.; Berrios, R.; Prieto, J. A. *Tetrahedron Lett.* **1989**, *30*, 283.

(256) Lohray, B. B.; Enders, D. *Helv. Chim. Acta* **1989**, *72*, 980.

(257) Enders, D.; Nakai, S. *Helv. Chim. Acta* **1990**, *73*, 1833.

(258) Cowden, C. J.; Paterson, I. In *Organic Reactions*; John Wiley&Sons, Inc.: **2004**.

(259) Enders, D.; Potthoff, M.; Raabe, G.; Runsink, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2362.

(260) Enders, D.; Hett, R. *Synlett* **1998**, 961.

(261) Enders, D.; Klein, D. *Synlett* **1999**, 719.

(262) Enders, D.; Oberborsch, S.; Adam, J. *Synlett* **2000**, 644.

(263) Enders, D.; Faure, S.; Potthoff, M.; Runsink, J. *Synthesis* **2001**, 2307.

(264) Enders, D.; Adam, J.; Oberborsch, S.; Ward, D. *Synthesis* **2002**, 2737.

(265) Enders, D.; Lohary, B. B. *Angew. Chem.* **1987**, *99*, 359.

(266) Bartoli, G.; Bosco, M.; Dalpozzo, R.; De, N. A.; Iantorno, E.; Tagarelli, A.; Palmieri, G. *Tetrahedron* **1996**, *52*, 9179.

(267) Corey, E. J.; Ruecker, C. *Tetrahedron Lett.* **1984**, *25*, 4345.

(268) Ge, M.; Corey, E. J. *Tetrahedron Lett.* **2006**, *47*, 2319.

(269) Obayashi, M.; Utimoto, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2646.

(270) Beisswenger, H.; Hanack, M. *Tetrahedron Lett.* **1982**, *23*, 403.

(271) Sato, S.; Matsuda, I.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 4229.

(272) Shen, R.; Corey, E. J. *Org. Lett.* **2007**, *9*, 1057.

(273) Demuth, M. *Helv. Chim. Acta* **1978**, *61*, 3136.

(274) Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. *Chem. Eur. J.* **2002**, *8*, 1730.

(275) Kondo, J.; Inoue, A.; Shinokubo, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2085.

(276) Cunico, R. F. *Tetrahedron Lett.* **1986**, *27*, 4269.

(277) Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. B* **1969**, 852.

(278) Miller, R. B.; Mcgarvey, G. *J. Org. Chem.* **1979**, *44*, 4623.

(279) Hoye, T. R.; Jeffrey, C. S.; Tennakoon, M. A.; Wang, J.; Zhao, H. *J. Am. Chem. Soc.* **2004**, *126*, 10210.

(280) Wang, X.; Bowman, E. J.; Bowman, B. J.; Porco, J. A., Jr. *Angew. Chem.* **2004**, *43*, 3601.

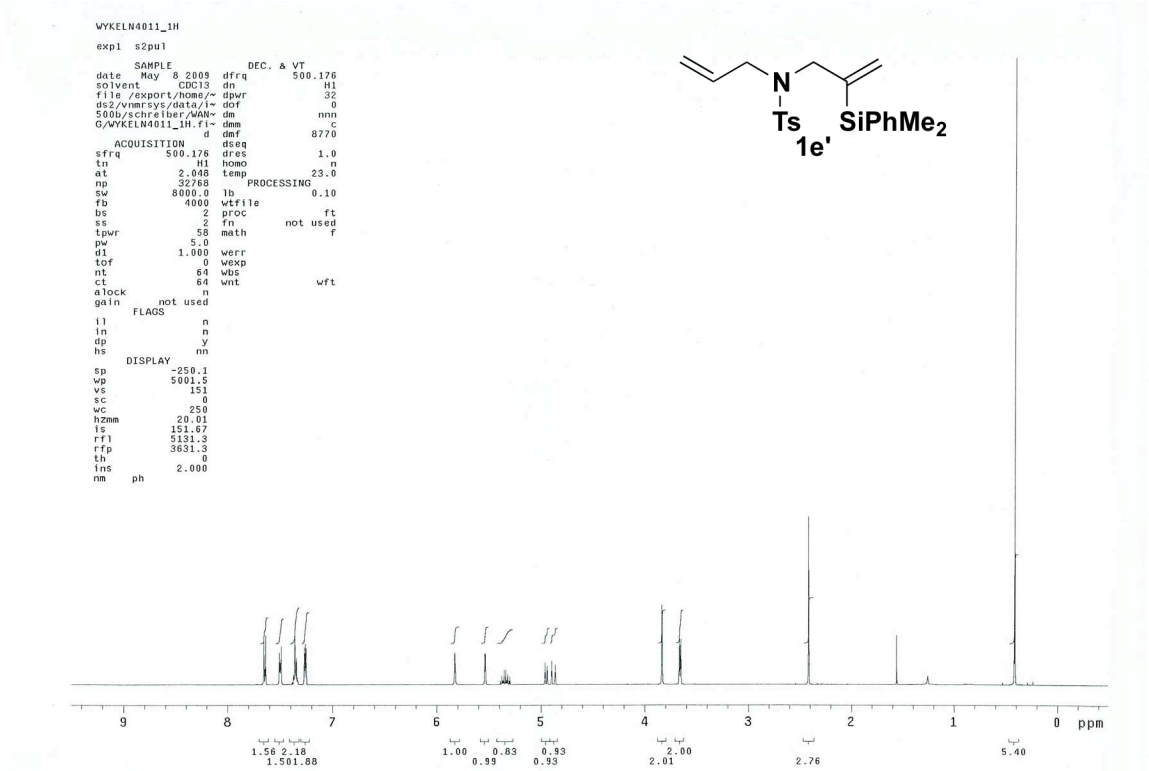
(281) Maifeld, S. V.; Lee, D. *Chemistry* **2005**, *11*, 6118.

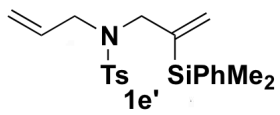
(282) Wallace, D. J. *Angew. Chem.* **2005**, *44*, 1912.

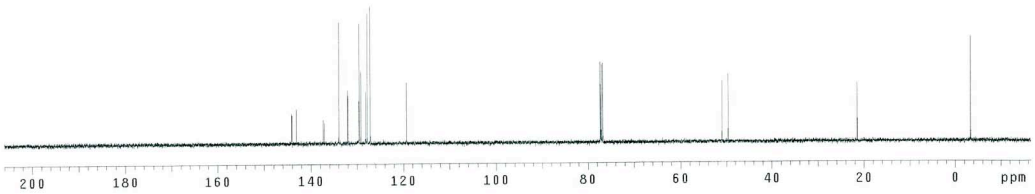
(283) Boeckman, R. K.; Blum, D. M.; Ganem, B.; Halvey, N. *Org. Synth.* **1988**, *50-9*, 1033.

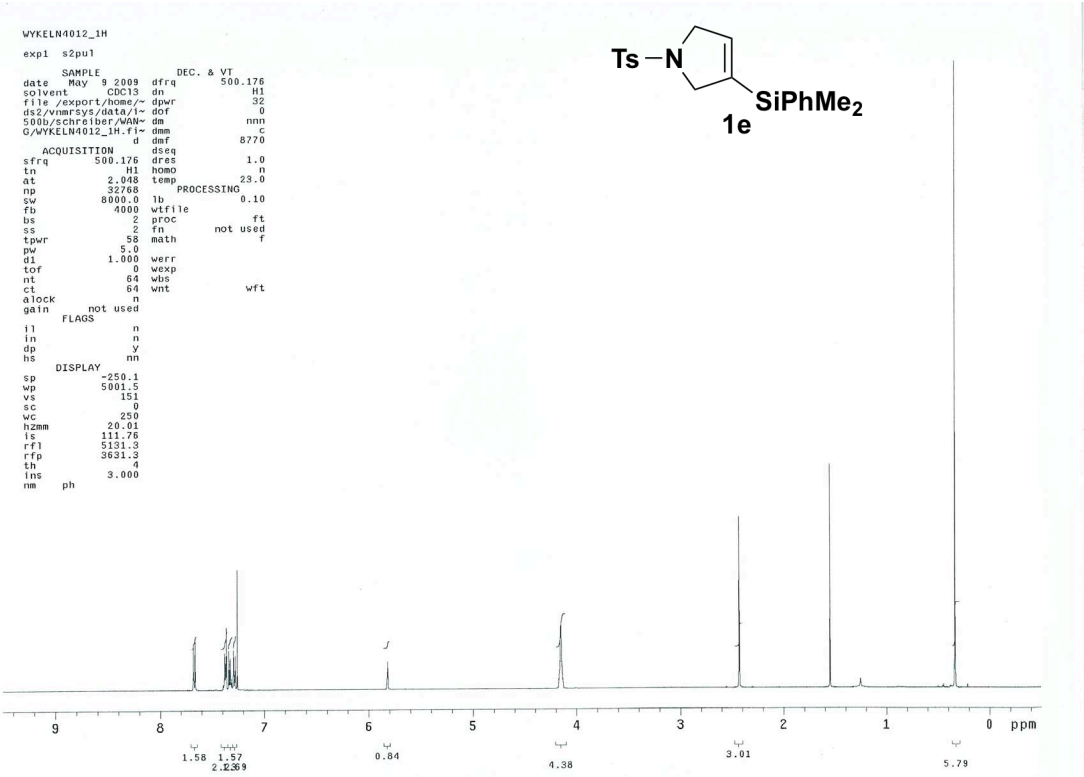
(284) Ilardi, E. A.; Stivala, C. E.; Zakarian, A. *Org. Lett.* **2008**, *10*, 1727.

^{1}H and ^{13}C NMR Spectra





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date May 9 2009
solvent CDCl3
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G/WYKELN4012_1H.fi~
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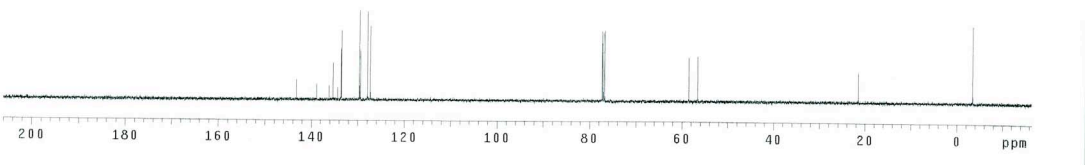
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 58
pw 5.0
d1 1.000
tof 0
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 111.76
rfl 5131.3
rfp 3631.3
th 4
ins 3.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Ts
N
SiPhMe2
1e
9
8
7
6
5
4
3
2
1
0
ppm
1.58
1.57
2.12
3.69
0.84
4.38
3.01
5.79


Ts
N
SiPhMe2
1e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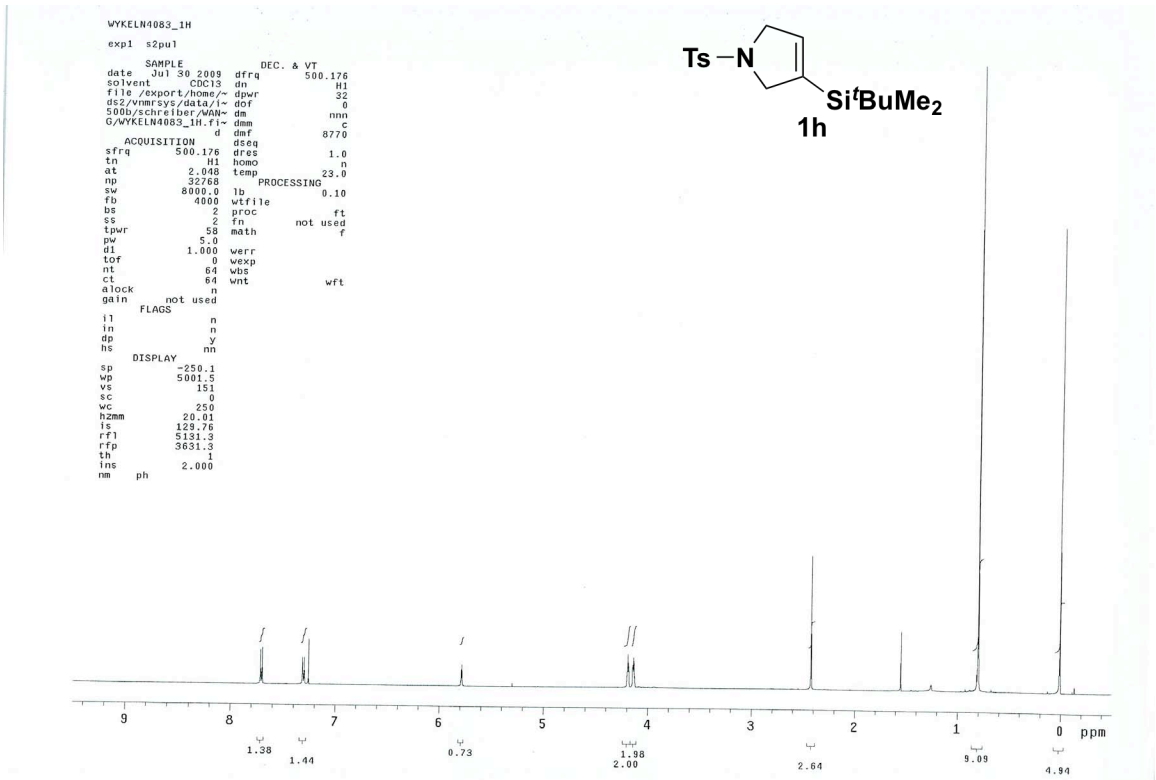
160
140
120
100
80
60
40
20
0
ppm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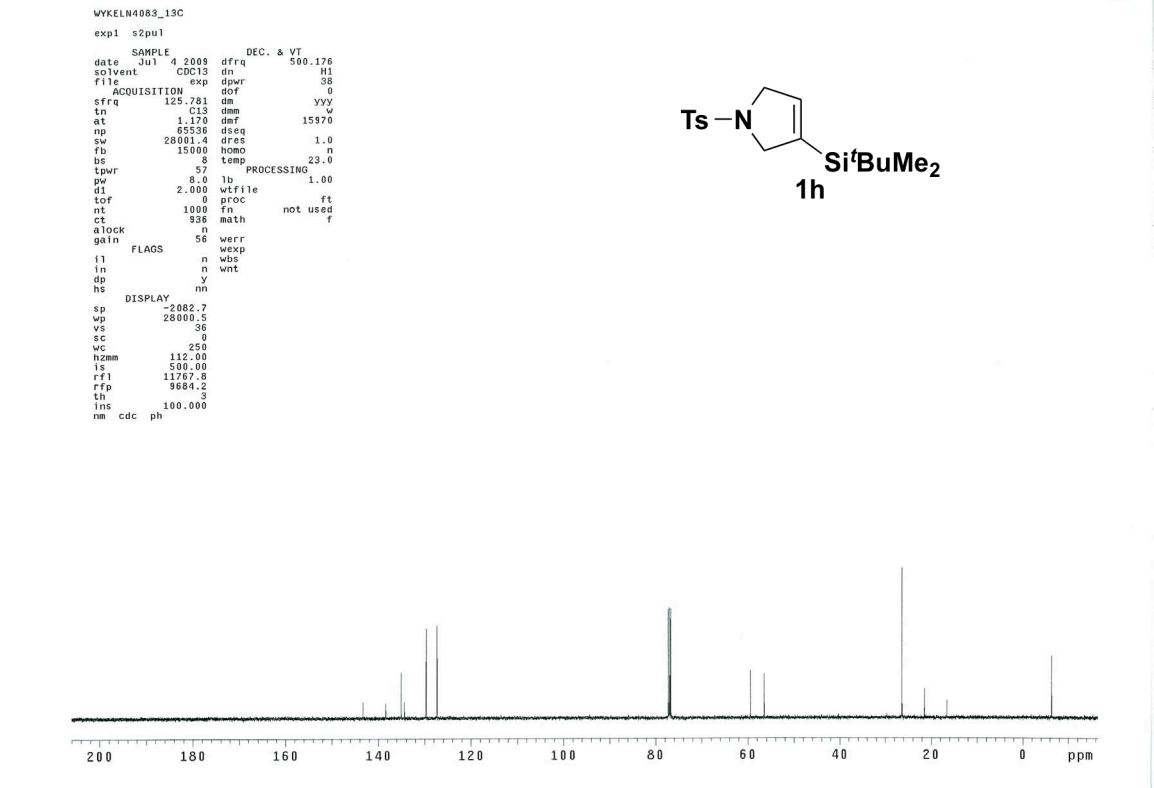
d
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 58
pw 5.0
d1 1.000
tof 0
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 129.76
rfl 5131.3
rfp 3631.3
th 1
ins 2.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Ts
N
Si^{t}BuMe$_2$
1h
9
8
7
6
5
4
3
2
1
0
ppm
1.38
1.44
0.73
1.98
2.00
2.64
9.09
4.94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solvent CDCl3
file exp
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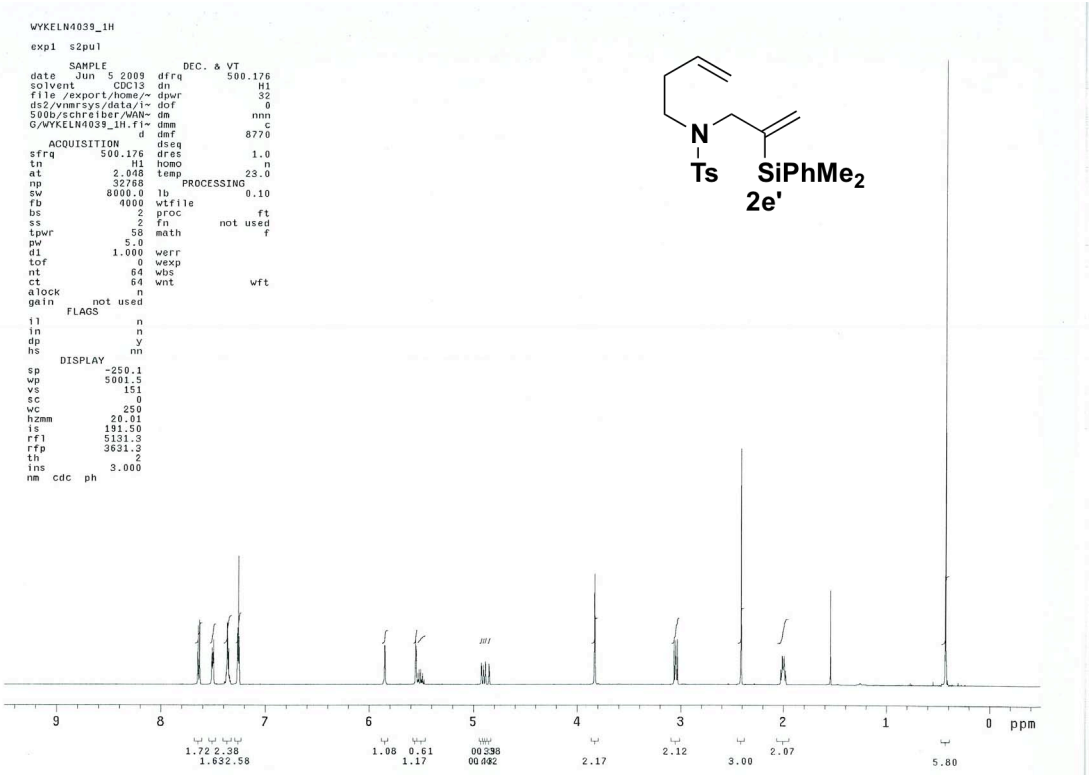
at 1.170
np 65536
sw 28001.4
fb 15000
bs 8
tpwr 57
pw 8.0
d1 2.000
tof 0
nt 1000
ct 936
alock n
gain 56
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2082.7
wp 28000.5
vs 36
sc 0
wc 250
hzmm 112.00
is 500.00
rfl 11767.8
rfp 9684.2
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 15970
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Ts
N
Si^{t}BuMe$_2$
1h
200
180
160
140
120
100
80
60
40
20
0
ppm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date Jun 5 2009
solvent CDCl3
file /export/home/~
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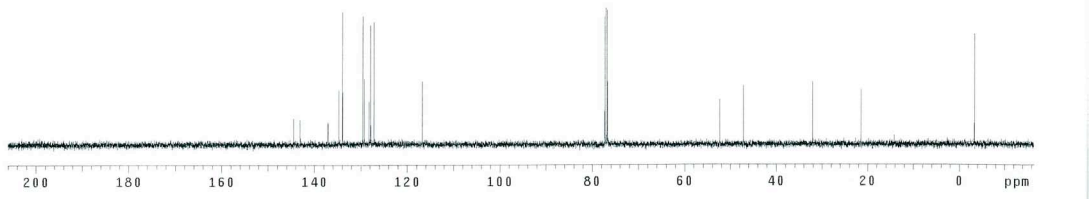
500b/schreiber/WAN~
G/WYKELN4039_1H.fi~
d
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 58
pw 5.0
d1 1.000
tof 0
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 191.50
rfl 5131.3
rfp 3631.3
th 2
ins 3.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
N
Ts
SiPhMe2
2e'
9
8
7
6
5
4
3
2
1
0 ppm
1.72 2.38
1.63 2.58
1.08 0.61
1.17
2.17
2.12
3.00
2.07
5.80


N
Ts
SiPhMe2
2e'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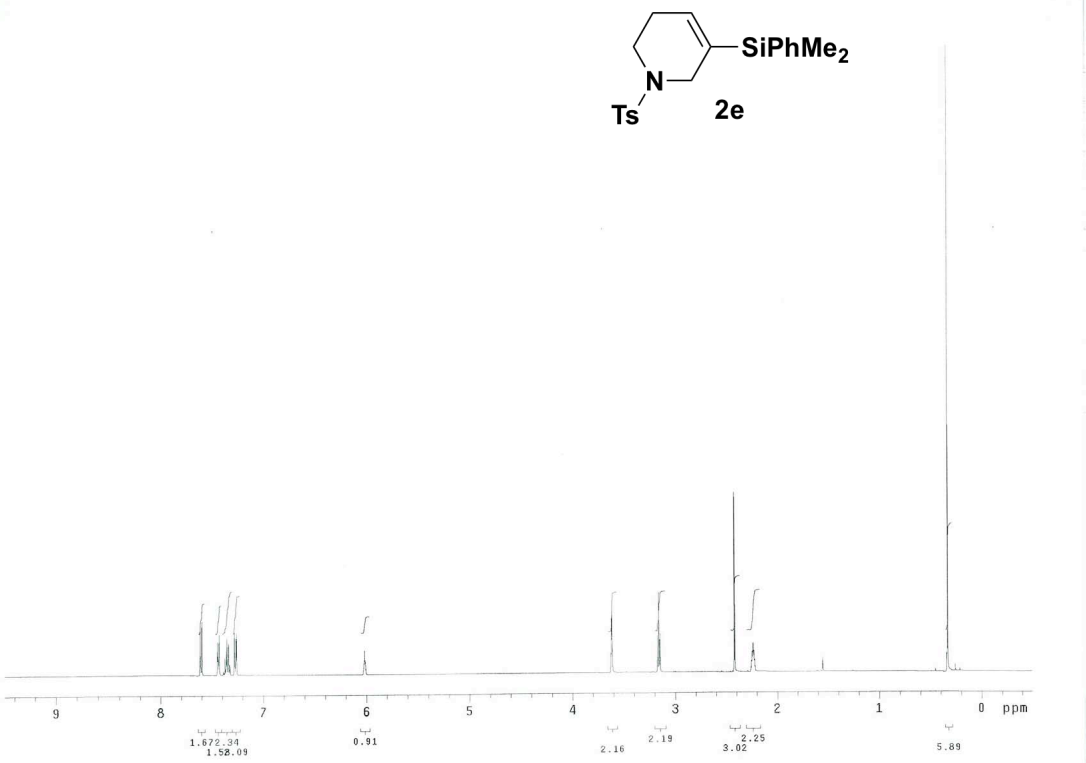
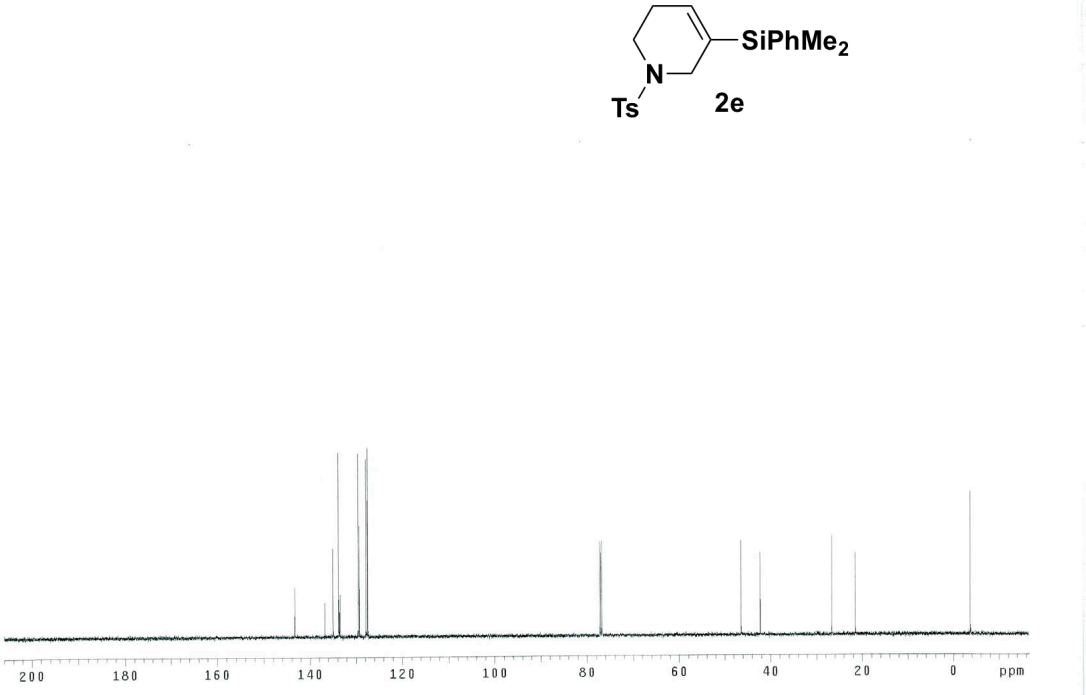
180
160
140
120
100
80
60
40
20
0 ppm


SiPhMe2
N
Ts
2e
9
8
7
6
5
4
3
2
1
0 ppm
1.67
2.34
1.58
0.91
2.16
2.19
2.25
3.02
5.89


SiPhMe2
N
Ts
2e
200
180
160
140
120
100
80
60
40
20
0
ppm

WYKELN4049_13C

expl s2pul

SAMPLE		DEC. & VT	
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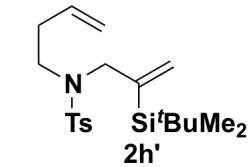
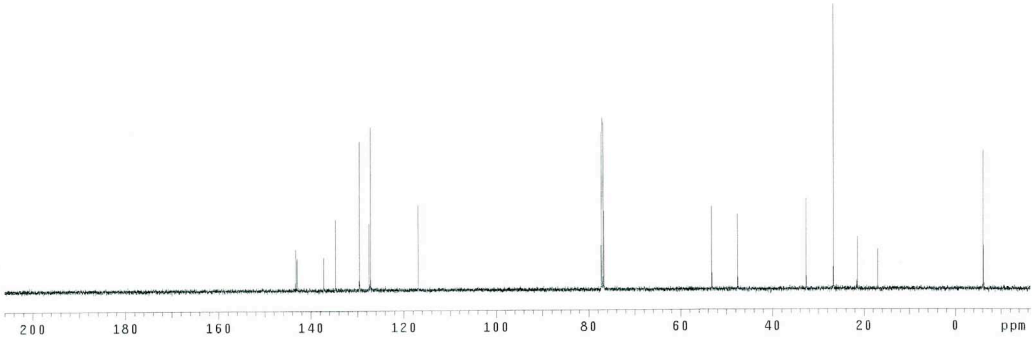
solvent	CDCl3	dn	H1
file	exp	dpwr	38
ACQUISITION		dof	0
sfrq	125.781	dm	yyy
tn	C13	dmm	w
at	1.170	dmf	15970
np	65536	dseq	
sw	28001.4	dres	1.0
fb	15000	homo	n
bs	8	temp	23.0
tpwr	57	PROCESSING	
pw	8.0	lb	1.00
dl	2.000	wtfile	
tof	0	proc	ft
nt	1000	fn	not used
ct	464	math	f
alock	n		
gain	56	werr	
FLAGS		wexp	
il	n	wbs	
in	n	wnt	
dp	y		
hs	nn		
DISPLAY			
sp	-2083.6		
wp	28000.5		
vs	69		
sc	0		
wc	250		
hzmm	112.00		
is	500.00		
rfl	11768.7		
rfp	9884.2		
th	3		
ins	100.000		

nm cdc ph



2h'



WYKELN1053_1H

expl s2pul

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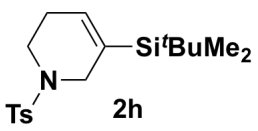
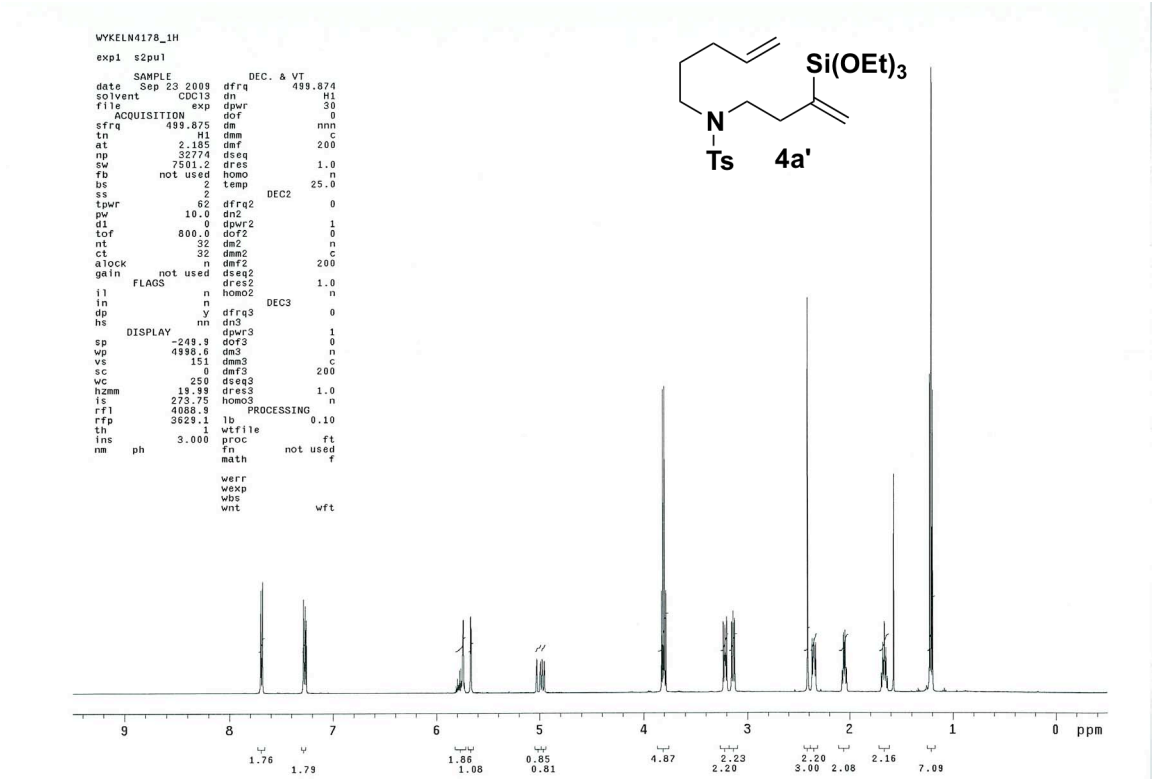
solvent	CDCl3	dn	H1
file	exp	dpwr	32
ACQUISITION		dof	0
sfrq	500.176	dm	nnn
tn	H1	dmm	c
at	2.048	dmf	8770
np	32768	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs	2	temp	23.0
ss	2	PROCESSING	
tpwr	58	lb	0.10
pw	5.0	wtfile	
dl	1.000	proc	ft
tof	0	fn	not used
nt	32	math	f
ct	32		
alock	n	werr	
gain	not used	wexp	
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5001.5		
vs	151		
sc	0		
wc	250		
hzmm	20.01		
is	1e+09		
rfl	1500.1		
rfp	0		
th	1		
ins	3.000		

nm cdc ph



2h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date Sep 23 2009
solvent CDCl3
file exp
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sfrq 499.875
tn H1
at 2.185
np 32774
sw 7501.2
fb not used
bs 2
ss 2
tpwr 62
pw 10.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.9
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 273.75
rfl 4088.9
rfp 3629.1
th 1
ins 3.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
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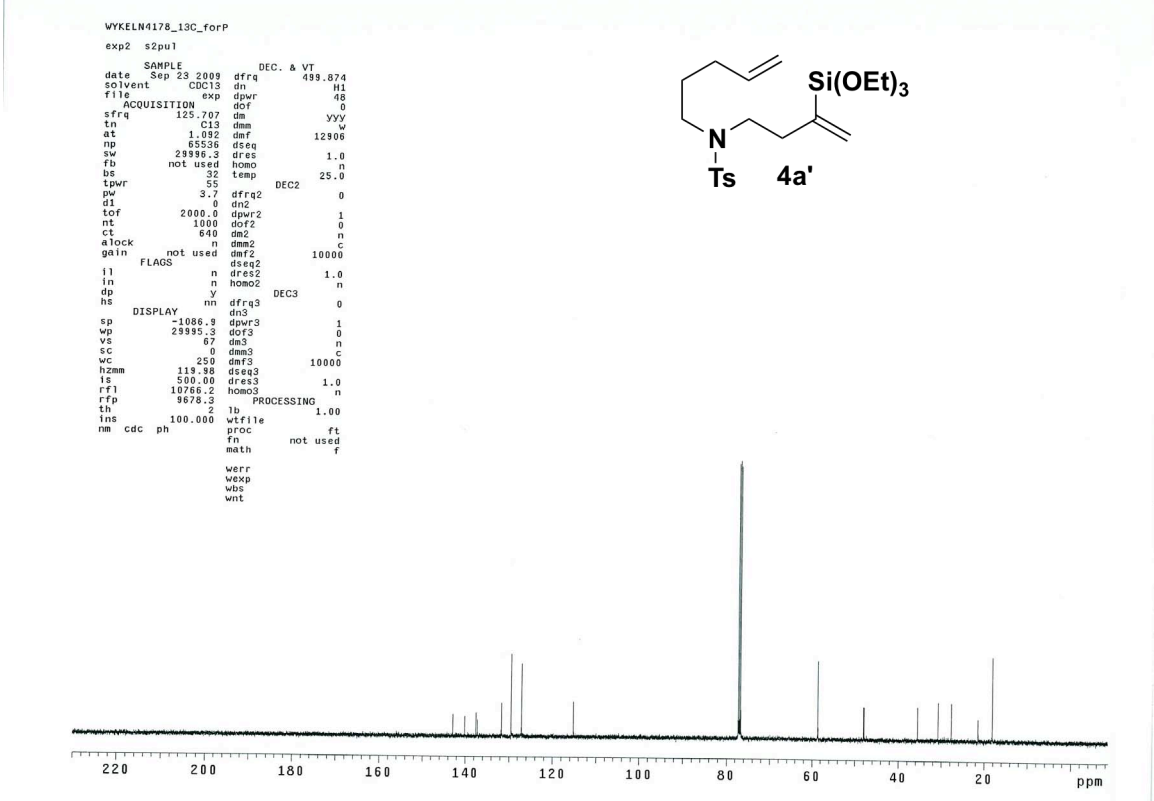
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Si(OEt)3
N
Ts
4a'
9
8
7
6
5
4
3
2
1
0
ppm
1.76
1.79
1.86
1.08
0.85
0.81
4.87
2.23
2.20
2.20
3.00
2.08
2.16
7.09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solvent CDCl3
file exp
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tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 3.7
d1 0
tof 2000.0
nt 1000
ct 640
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1086.9
wp 29995.3
vs 67
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10766.2
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
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dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 12906
dseq
dres 1.0
homo n
temp 25.0
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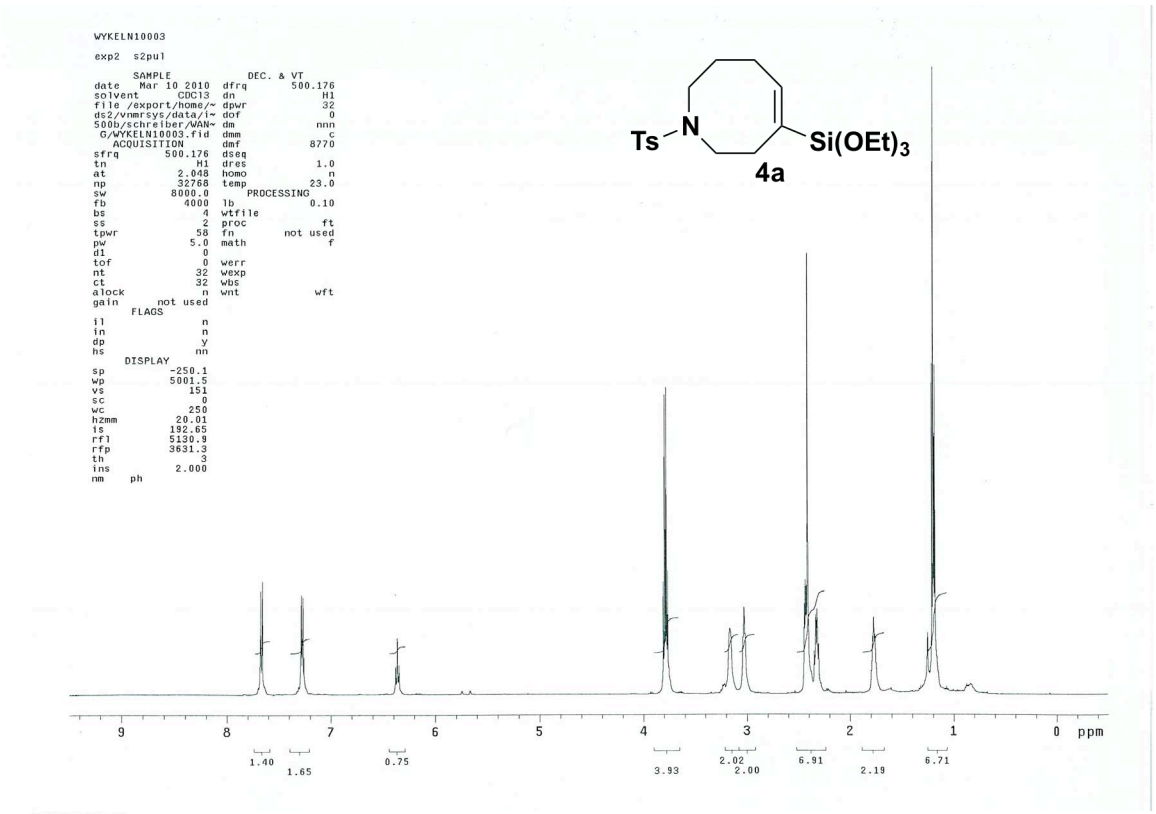
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Si(OEt)3
N
Ts
4a'
220
200
180
160
140
120
100
80
60
40
20
ppm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SAMPLE
date Mar 10 2010
solvent CDCl3
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500b/schreiber/WAN~
G/WYKELN10003.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 192.65
rfl 5130.9
rfp 3631.3
th 3
ins 2.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dof 32
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Ts
N
Si(OEt)3
4a
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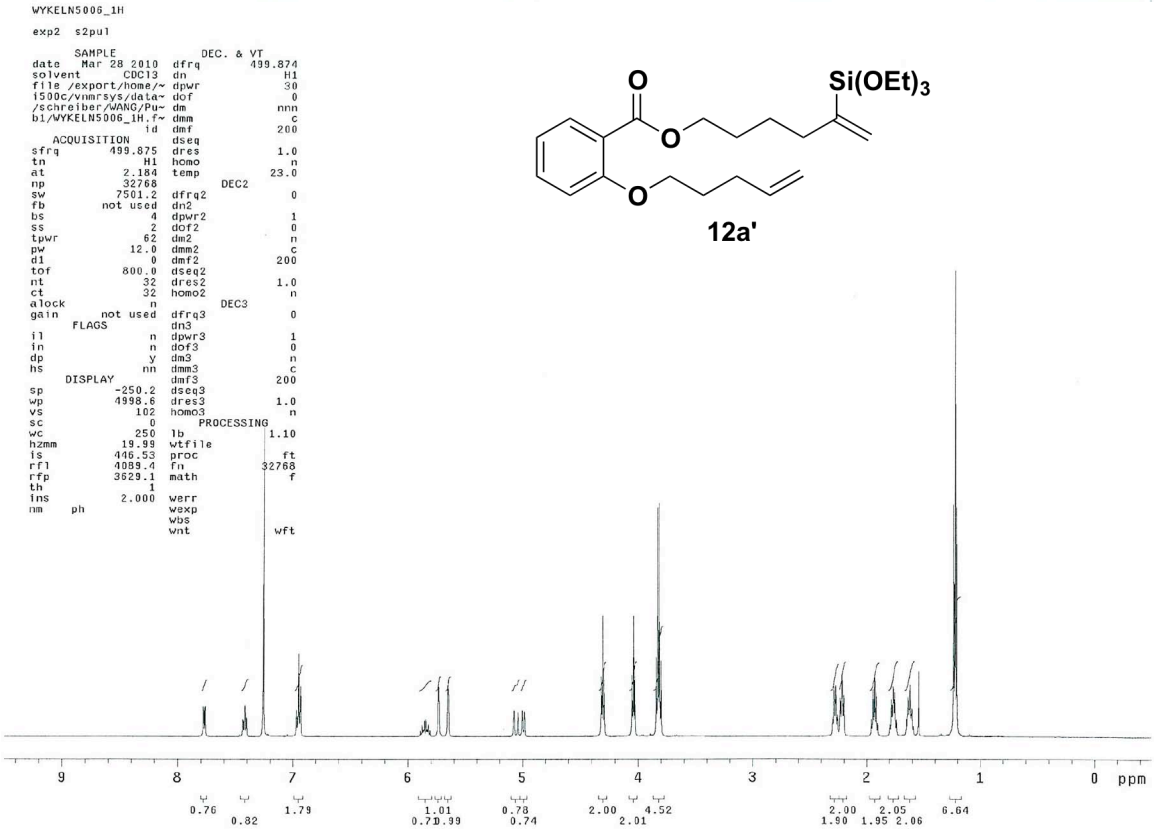
1.40 1.65 0.75 3.93 2.02 2.00 6.91 2.19 6.71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exp2 s2pul
SAMPLE
date Mar 28 2010
solvent CDCl3
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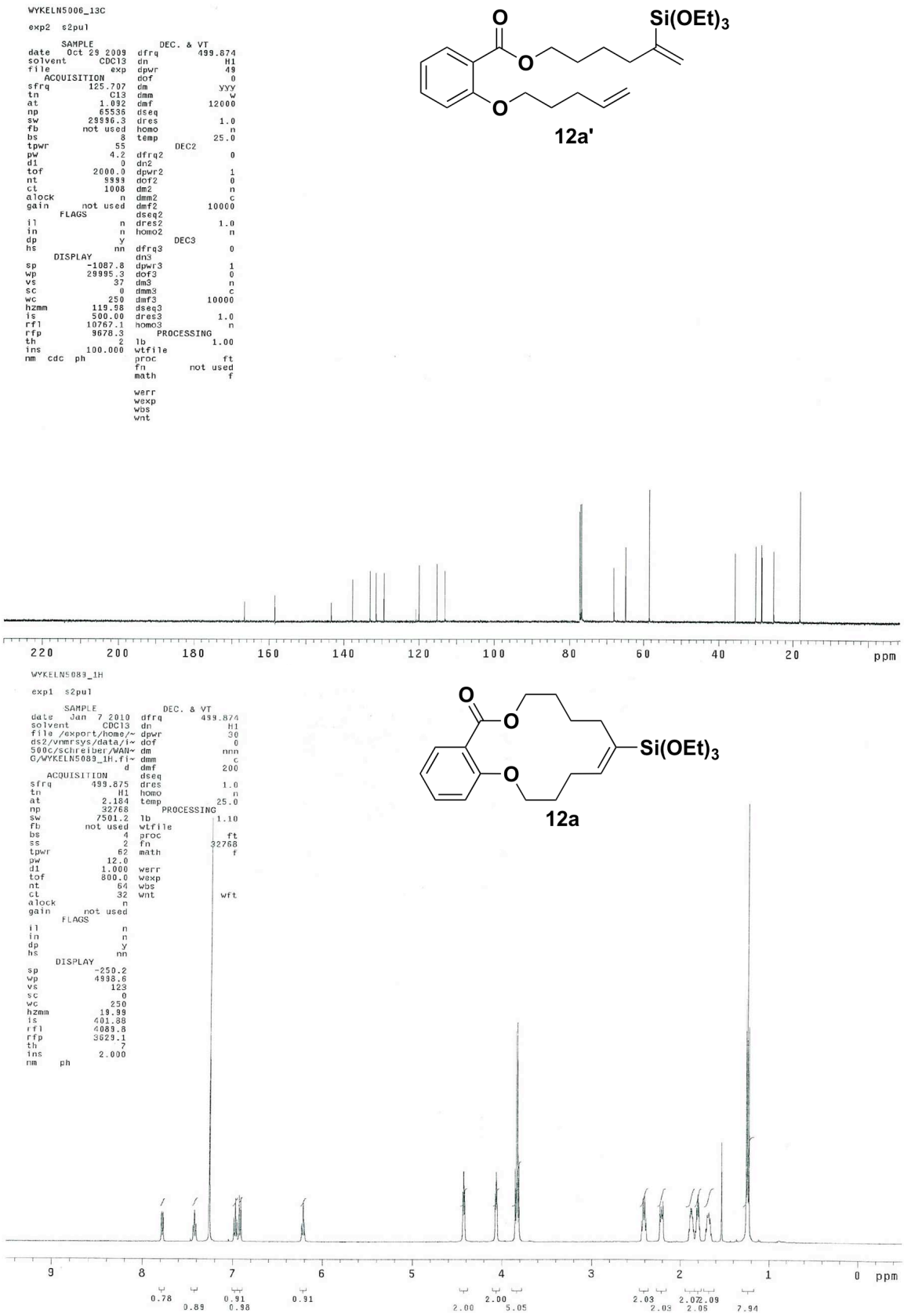
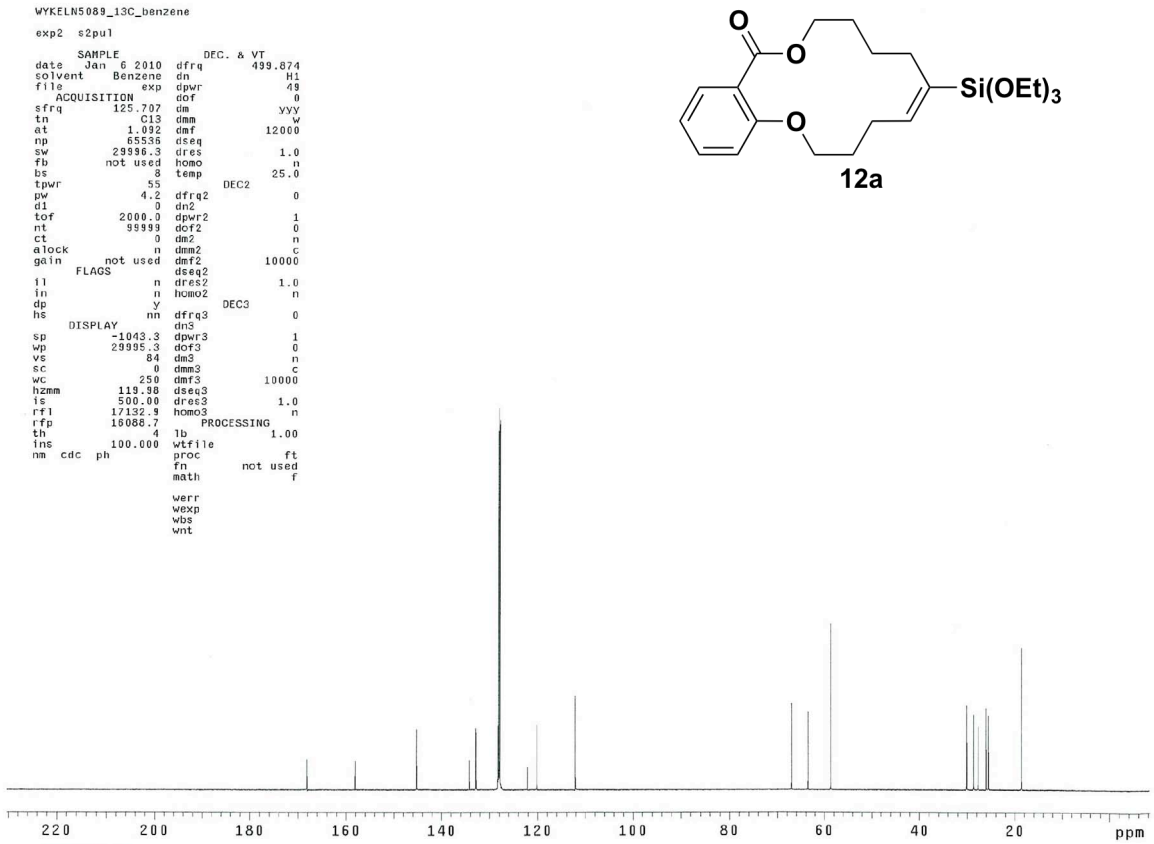
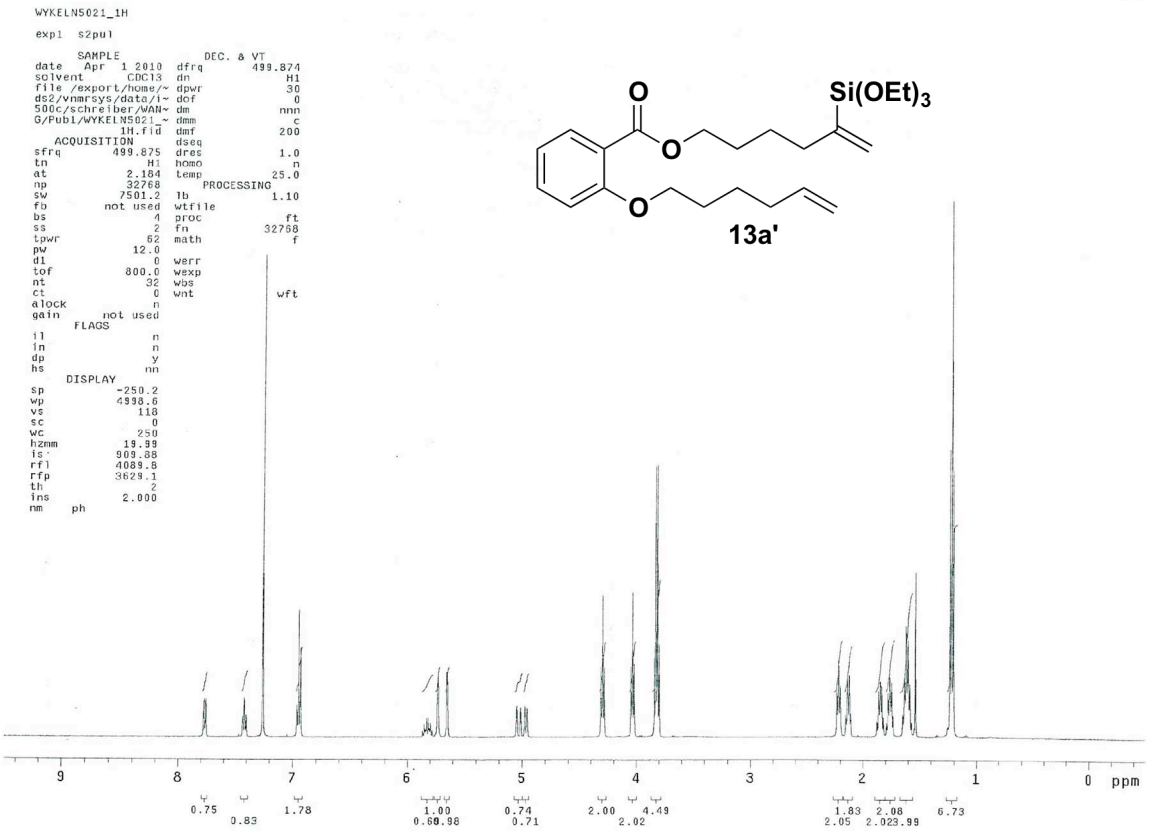
/schreiber/WANG/Pu~
b1/WYKELN5006_1H.f~
id
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 102
sc 0
wc 250
hzmm 19.98
is 446.53
rfl 4089.4
rfp 3629.1
th 1
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 23.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)3
12a'
9 8 7 6 5 4 3 2 1 0 ppm
0.76 0.82 1.79 1.01 0.71 0.99 0.78 0.74 2.00 4.52 2.01 2.00 1.80 2.05 1.95 2.06 6.64


WYKELN5006_13C
exp2 s2pul
SAMPLE
date Oct 29 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 8
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 9999
ct 1008
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 37
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 49
dof 0
dm yyy
dmm w
dmf 12000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)3
12a'
220
200
180
160
140
120
100
80
60
40
20
ppm
WYKELN5089_1H
exp1 s2pul
SAMPLE
date Jan 7 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/WYKELN5089_1H.fi~
d
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 1.000
tof 800.0
nt 64
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 123
sc 0
wc 250
hzmm 19.99
is 401.88
rfl 4089.8
rfp 3629.1
th 7
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)3
12a
9
8
7
6
5
4
3
2
1
0
ppm
0.78
0.89
0.91
0.98
0.91
2.00
2.00
5.05
2.03
2.03
2.07
2.05
2.09
7.94

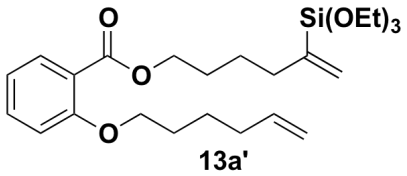

WYKELN5089_13C_benzene
exp2 s2pul
SAMPLE
date Jan 6 2010
solvent Benzene
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 8
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1043.3
wp 29995.3
vs 84
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 17132.9
rfp 18088.7
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 49
dof 0
dm yyy
dmm w
dmf 12000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)3
12a
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN5021_1H
exp1 s2pul
SAMPLE
date Apr 1 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN5021_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 118
sc 0
wc 250
hzmm 19.99
is 909.88
rfl 4089.6
rfp 3629.1
th 2
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)3
13a'
9
8
7
6
5
4
3
2
1
0
ppm
0.75
0.83
1.78
1.00
0.60
0.98
0.74
0.71
2.00
2.02
4.49
1.83
2.05
2.08
2.02
3.99
6.73

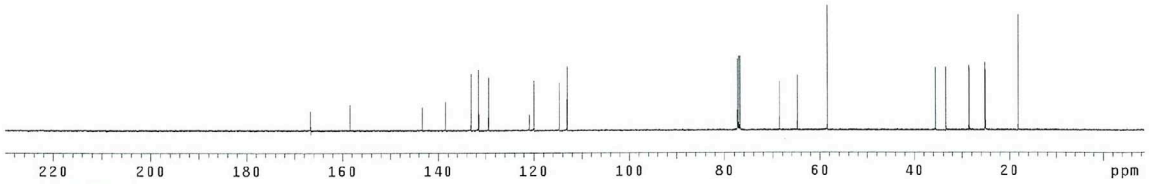
WYKELN5021_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 1 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	0	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1089.7	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.9	homo3	n
rfp	9678.3	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



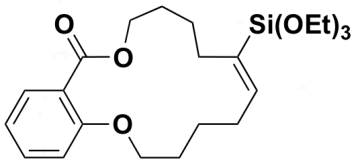
13a'



WYKELN10001_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 5 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/i~	dof	0
	500c/schreiber/WAN~	dm	nnn
	G/Pub1/WYKELN10001~	dmm	c
	1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0	werr	
d1	0	wexp	
tof	800.0	wbs	
nt	32	wnt	wft
ct	32		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	139		
sc	0		
wc	250		
hzmm	19.99		
is	345.32		
rfl	4089.8		
rfp	3629.1		
th	5		
ins	2.000		
nm ph			

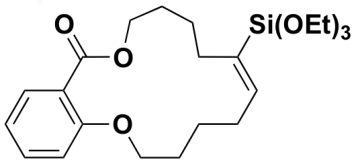


13a

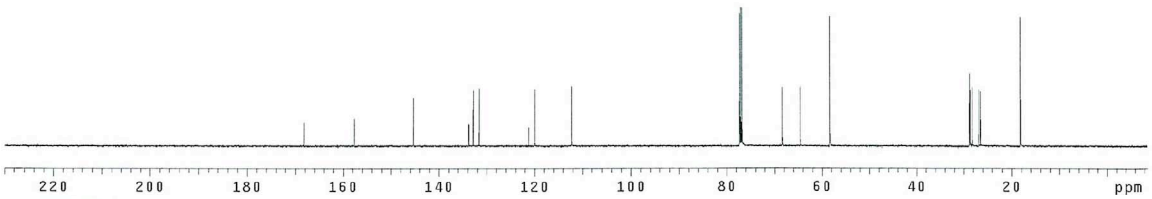
WYKELN10001_13C

exp4 s2pul

SAMPLE		DEC. & VT	
date	Apr 5 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	2112	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1088.7	dpwr3	1
wp	29995.3	dof3	0
vs	30	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.0	homo3	n
rfp	9678.3	PROCESSING	
th	8	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



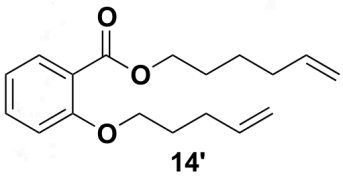
13a



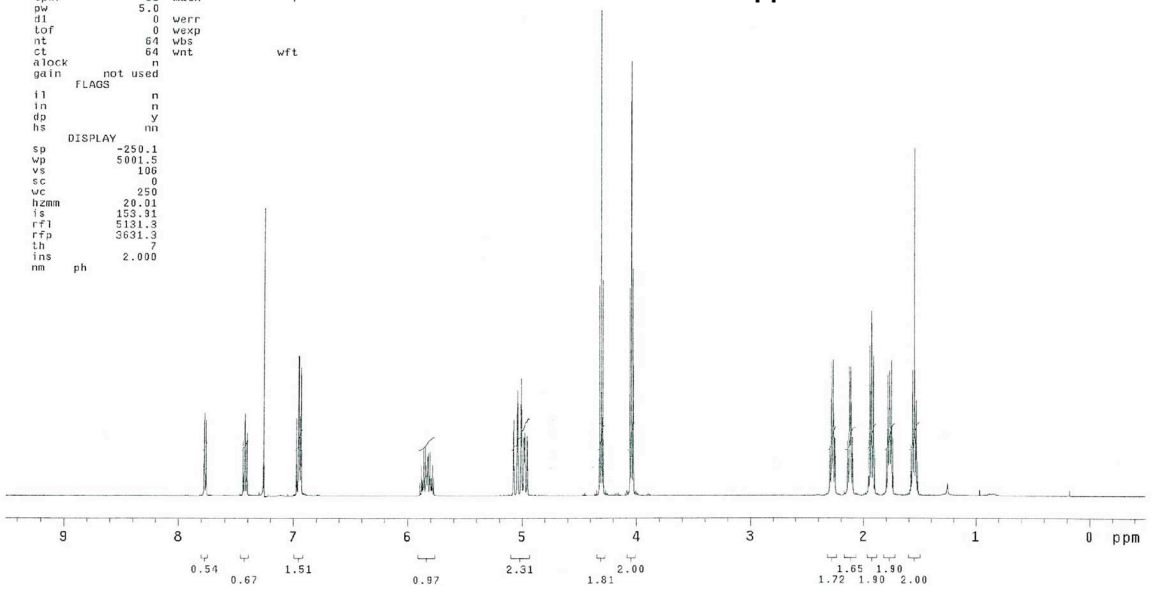
WYKELN5009_1H

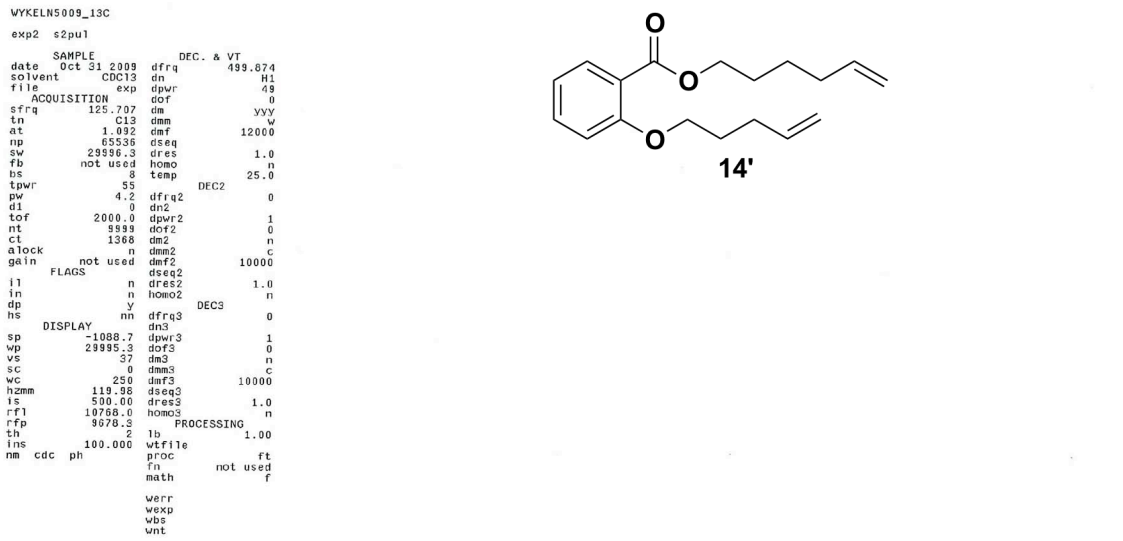
exp1 s2pul

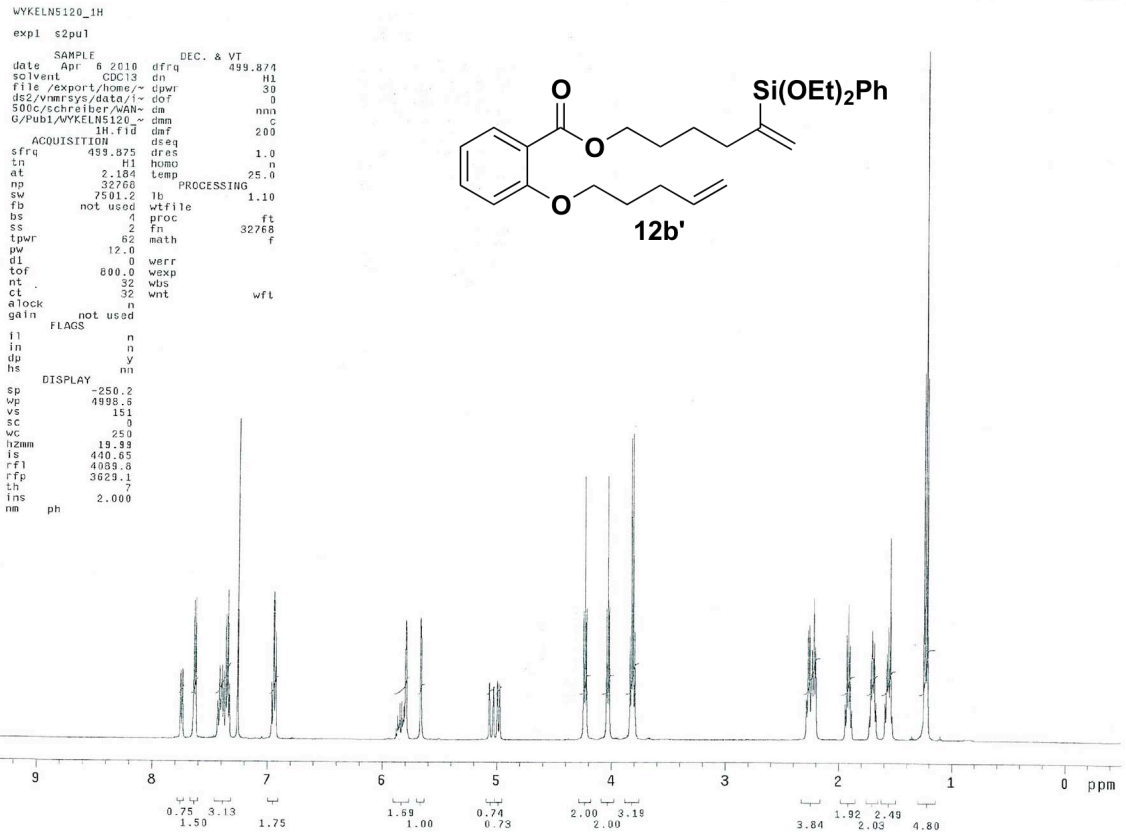
SAMPLE		DEC. & VT	
date	Oct 31 2009	dfrq	500.176
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	32
	ds2/vnmrsys/data/i~	dof	0
	500b/schreiber/WAN~	dm	nnn
	G/WYKELN5009_1H.fi~	dmm	c
	d	dmf	8770
ACQUISITION		dseq	
sfrq	500.176	dres	1.0
tn	H1	homo	n
at	2.048	temp	23.0
np	32768	PROCESSING	
sw	8000.0	lb	0.10
fb	4000	wtfile	
bs	2	proc	ft
ss	2	fn	not used
tpwr	58	math	f
pw	5.0	werr	
d1	0	wexp	
tof	0	wbs	
nt	64	wnt	wft
ct	64		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5001.5		
vs	106		
sc	0		
wc	250		
hzmm	20.01		
is	153.31		
rfl	5131.3		
rfp	3631.3		
th	7		
ins	2.000		
nm ph			

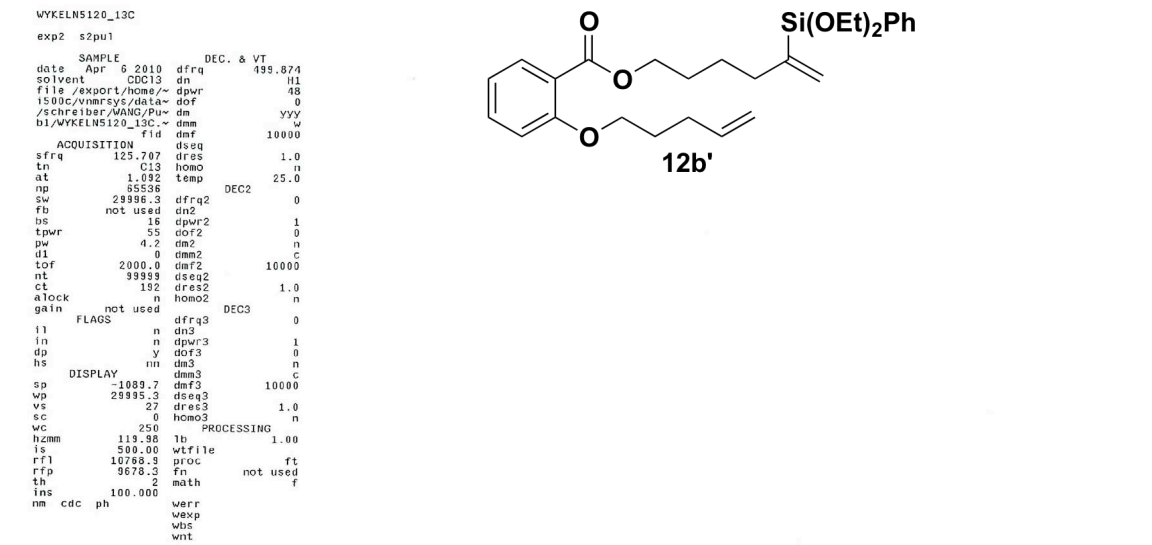


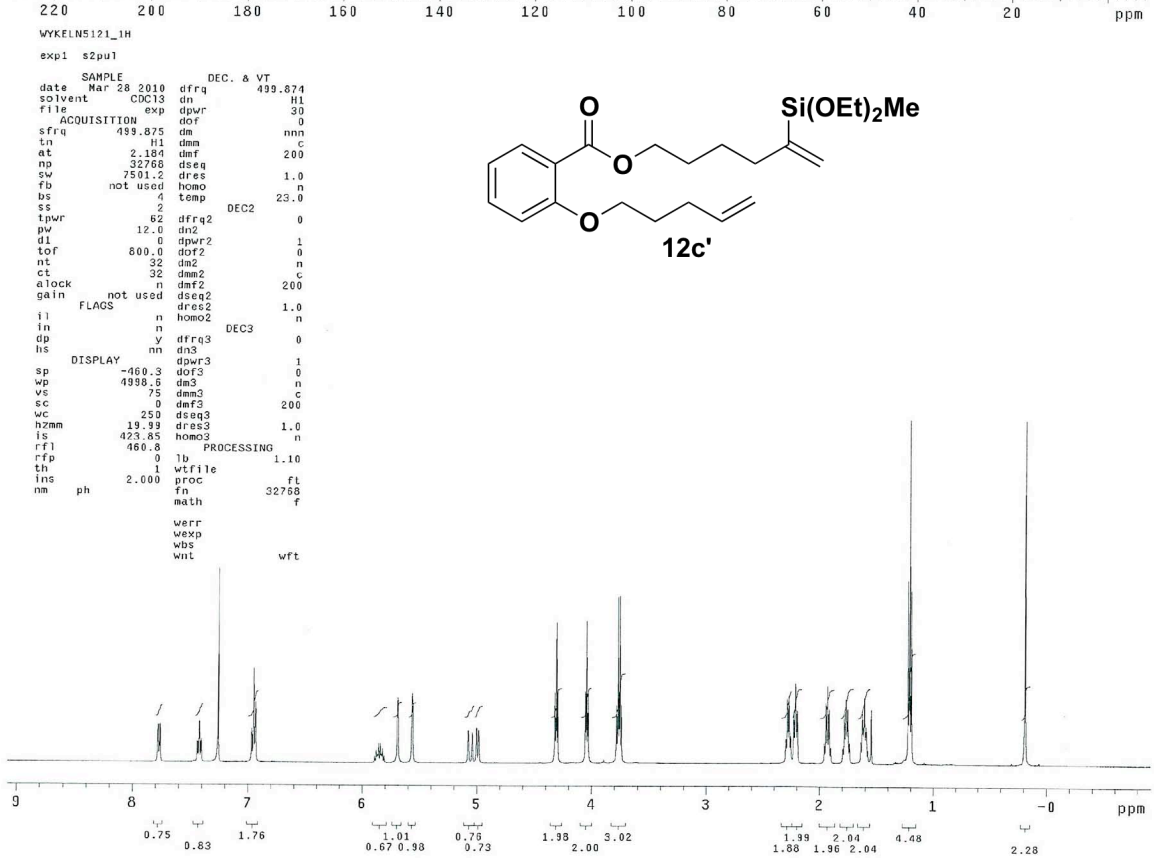
14'

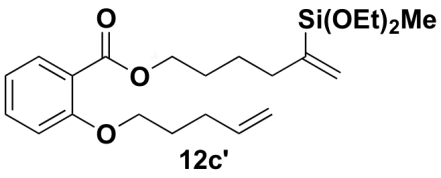



WYKELN5009_13C
exp2 s2pul
SAMPLE
date Oct 31 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 8
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 9999
ct 1368
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1088.7
wp 29995.3
vs 37
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.0
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 49
dof 0
dm yyy
dmm w
dmf 12000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
14'
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN5120_1H
exp1 s2pul
SAMPLE
date Apr 6 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500c/schreiber/WAN~
G/Publ/WYKELN5120_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.5
vs 151
sc 0
wc 250
hzmm 19.99
is 440.65
rfl 4089.8
rfp 3623.1
th 7
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Ph
12b'
9
8
7
6
5
4
3
2
1
0
ppm
0.75
3.13
1.50
1.75
1.59
1.00
0.74
0.73
2.00
3.19
2.00
3.84
1.92
2.49
2.03
4.80

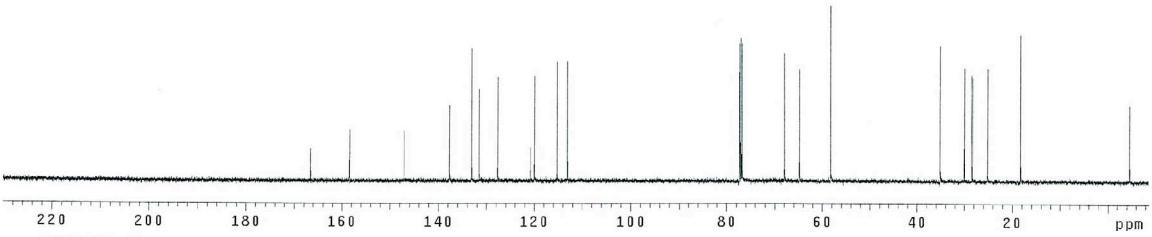

WYKELN5120_13C
exp2 s2pul
SAMPLE
date Apr 6 2010
solvent CDCl3
file /export/home/~
i500c/vnmrsys/data~
/schreiber/WANG/Pu~
b1/WYKELN5120_13C.~
fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 192
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1089.7
wp 29995.3
vs 27
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.9
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)2Ph
12b'
220
200
180
160
140
120
100
80
60
40
20
ppm

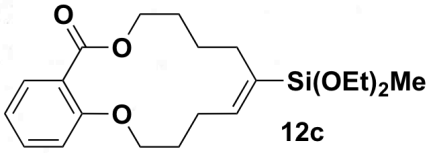

WYKELN5121_1H
exp1 s2pul
SAMPLE
date Mar 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -460.3
wp 4998.6
vs 75
sc 0
wc 250
hzmm 19.99
is 423.85
rfl 460.8
rfp 0
th 1
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 23.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
12c'
9
8
7
6
5
4
3
2
1
-0
ppm
0.75
0.83
1.76
1.01
0.67 0.98
0.76
0.73
1.98
2.00
3.02
1.99
1.88
2.04
1.96
2.04
4.48
2.28



12c'

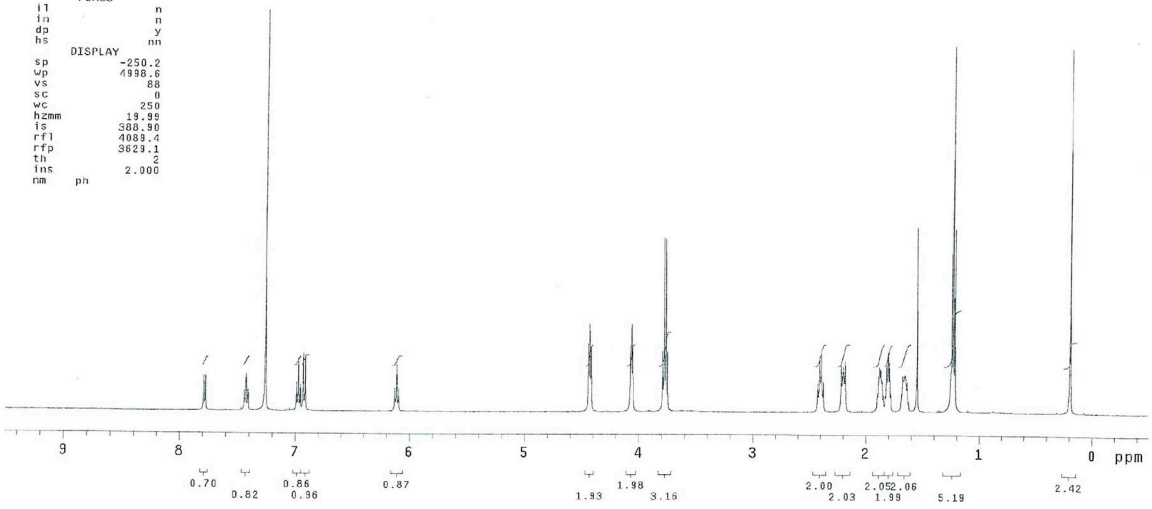
```
WYKELN5121_13C

exp1  s2pul

      SAMPLE                DEC. & VT
date   Mar 28 2010  dfrq        499.874
solvent       CDCl3  dn              H1
file            exp  dpwr            48
    ACQUISITION      dof              0
sfrq        125.707  dm             yyy
tn              C13  dmm              w
at            1.092  dmf          10000
np            65536  dseq
sw          29996.3  dres           1.0
fb        not used   homo             n
bs              16   temp          23.0
tpwr            55        DEC2
pw             4.2   dfrq2            0
d1               0   dn2
tof         2000.0   dpwr2            1
nt            9999   dof2             0
ct             384   dm2              n
alock            n   dmm2             c
gain      not used   dmf2         10000
      FLAGS         dseq2
il               n   dres2          1.0
in               n   homo2            n
dp               y        DEC3
hs              nn   dfrq3            0
     DISPLAY         dn3
sp         -1090.6   dpwr3            1
wp         29995.3   dof3             0
vs              38   dm3              n
sc               0   dmm3             c
wc             250   dmf3         10000
hzmm         119.98  dseq3
is           500.00  dres3          1.0
rfl         10769.8  homo3            n
rfp          9678.3       PROCESSING
th               6   lb             1.00
ins          100.000 wtfile
nm  cdc  ph          proc             ft
                     fn         not used
                     math              f

                     werr
                     wexp
                     wbs
                     wnt
```





12c

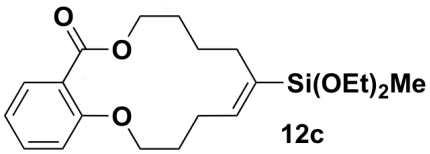
```
WYKELN10013_1H

exp1  s2pul

      SAMPLE                DEC. & VT
date   Mar 31 2010  dfrq        499.874
solvent       CDCl3  dn              H1
file /export/home/~  dpwr            30
ds2/vnmrsys/data/i~  dof              0
500c/schraiber/NMR~  dm             nnn
G/Publ/WYKELN10013~  dmm              c
          _1H.fid    dmf            200
    ACQUISITION      dseq
sfrq        499.875  dres           1.0
tn              H1   homo             n
at           2.184        PROCESSING
np           32768   lb             1.10
sw          7501.2   wtfile
fb        not used   proc             ft
bs               4   fn             32768
ss               2   math              f
tpwr            62
pw            12.0   werr
d1               0   wexp
tof          800.0   wbs
nt              32   wnt              wft
ct              32
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              nn
     DISPLAY
sp          -250.2
wp          4998.6
vs              88
sc               0
wc             250
hzmm         19.99
is           388.90
rfl         4089.4
rfp         3629.1
th               2
ins          2.000
nm    ph
```



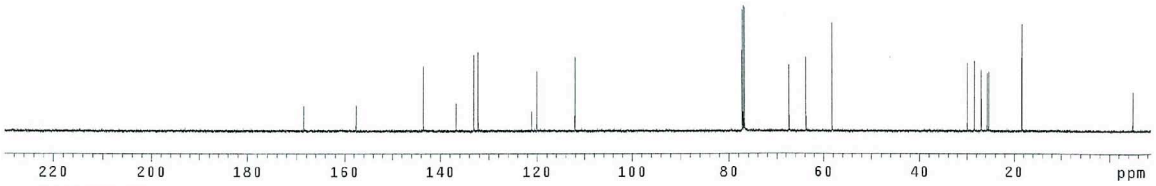
WYKELN10013_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Mar 31 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	DEC2	
tpwr	55	dfrq2	0
pw	4.2	dn2	
d1	0	dpwr2	1
tof	2000.0	dof2	0
nt	9999	dm2	n
ct	560	dmm2	c
alock	n	dmf2	10000
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-1090.6	dof3	0
wp	29995.3	dm3	n
vs	27	dmm3	c
sc	0	dmf3	10000
wc	250	dseq3	
hzmm	119.98	dres3	1.0
is	500.00	homo3	n
rfl	10769.8	PROCESSING	
rfp	9678.3	lb	1.00
th	3	wtfile	
ins	100.000	proc	ft
nm cdc ph		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



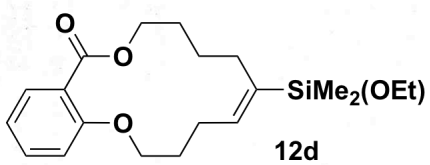
12c



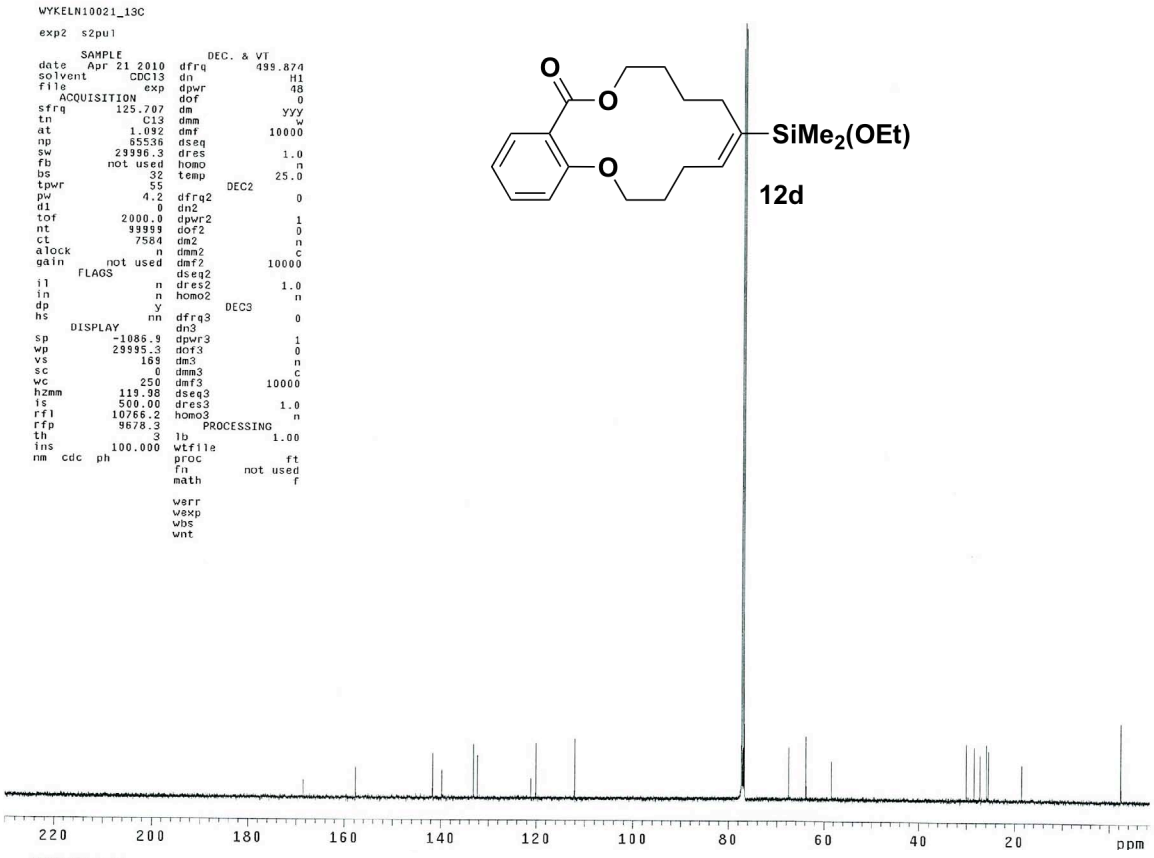
WYKELN10021_1H

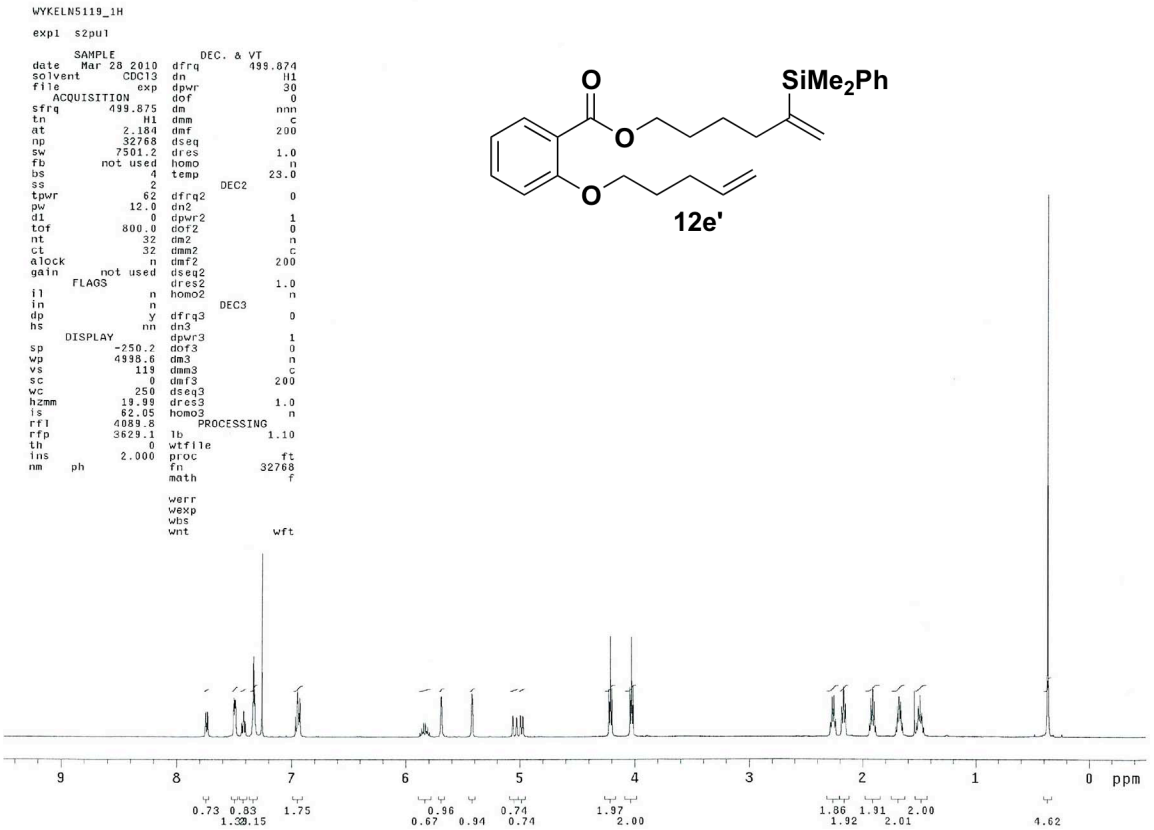
exp1 s2pul

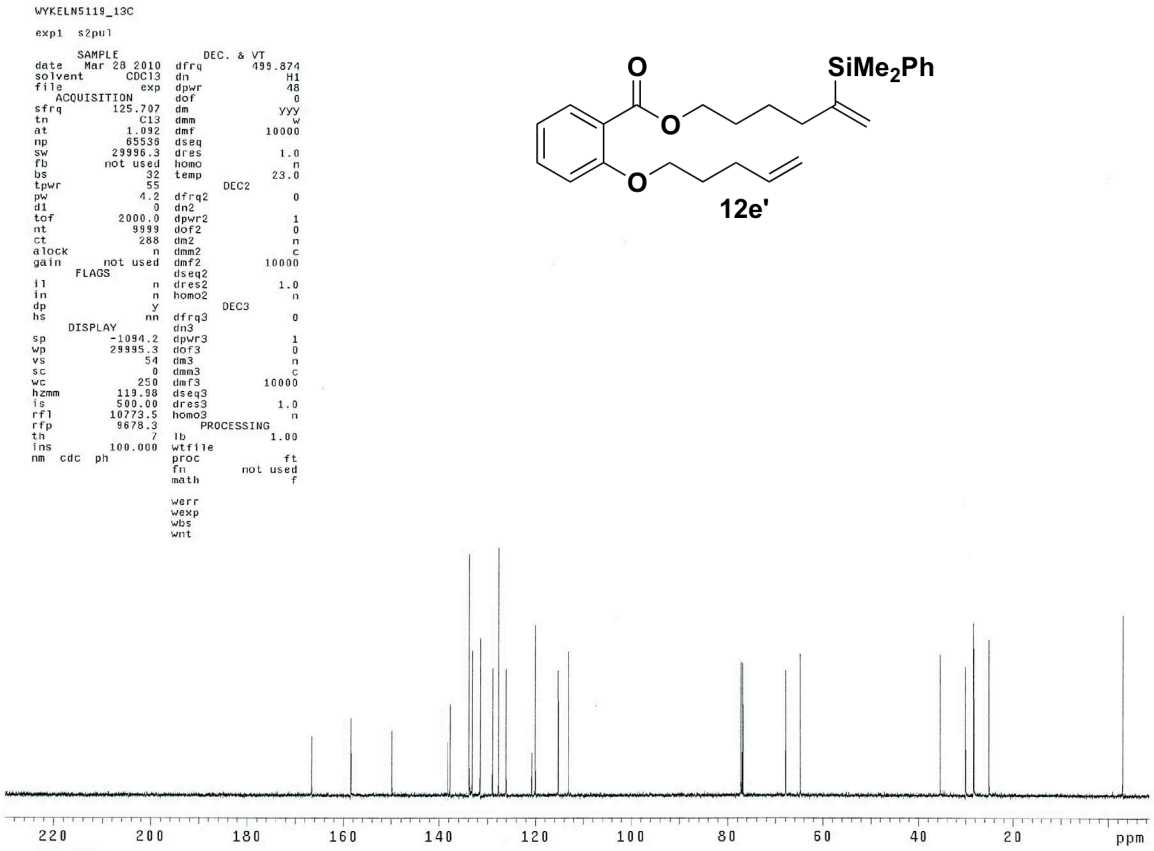
SAMPLE		DEC. & VT	
date	Apr 21 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
ds2/vnmrsys/data/i~		dof	0
500c/schreiber/WAN~		dm	nnn
G/Pub1/WYKELN10021~		dmm	c
	_1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	32	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-259.8		
wp	4998.6		
vs	148		
sc	0		
wc	259		
hzmm	19.99		
is	177.83		
rfl	4089.8		
rfp	3629.1		
th	7		
ins	2.000		
nm ph			

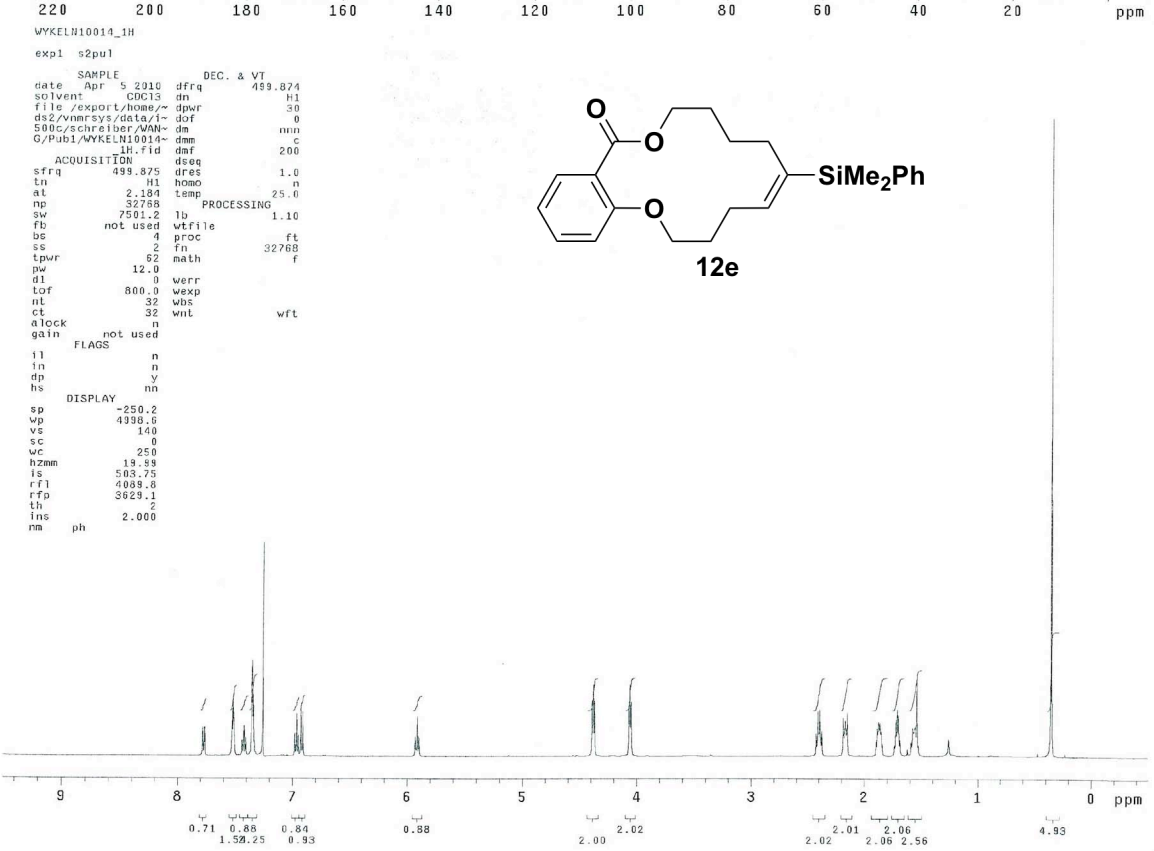


12d


WYKELN10021_13C
exp2 s2pul
SAMPLE
date Apr 21 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 7584
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1086.9
wp 29995.3
vs 169
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10766.2
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
SiMe2(OEt)
12d
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN5119_1H
exp1 s2pul
SAMPLE
date Mar 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 119
sc 0
wc 250
hzmm 19.99
is 82.05
rfl 4089.8
rfp 3629.1
th 0
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 23.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
SiMe2Ph
12e'
9
8
7
6
5
4
3
2
1
0 ppm
0.73 0.83 1.75
1.33 3.15
0.96
0.67 0.94
0.74
0.74
1.97
2.00
1.86 1.91 2.00
1.92 2.01
4.62

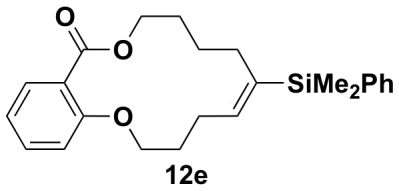

WYKELN5119_13C
exp1 s2pul
SAMPLE
date Mar 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 9999
ct 288
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1094.2
wp 29995.3
vs 54
sc 0
wc 250
hzmm 119.88
is 500.00
rfl 10773.5
rfp 9678.3
th 7
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 23.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
SiMe2Ph
12e'
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN10014_1H
exp1 s2pul
SAMPLE
date Apr 5 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500c/schreiber/WAN~
G/Pub1/WYKELN10014~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 52
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 140
sc 0
wc 250
hzmm 19.99
is 503.75
rfl 4089.8
rfp 3629.1
th 2
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
SiMe2Ph
12e
9
8
7
6
5
4
3
2
1
0
ppm
0.71
0.88
1.52
0.25
0.84
0.93
0.88
2.00
2.02
2.02
2.01
2.06
2.06
2.56
4.93

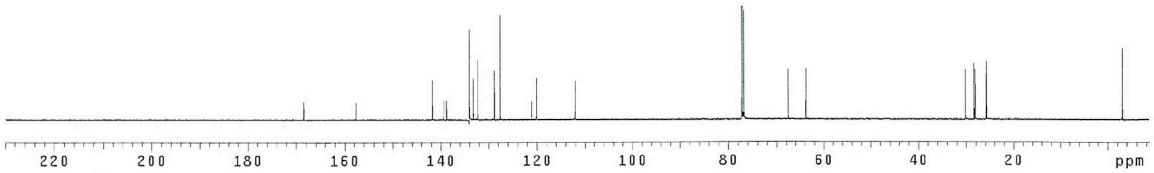
WYKELN10014_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 2 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29936.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	2128	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1088.7	dpwr3	1
wp	29995.3	dof3	0
vs	25	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.0	homo3	n
rfp	9678.3	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



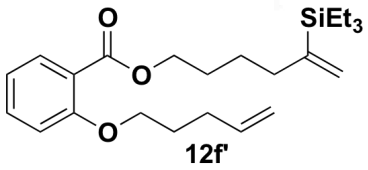
12e



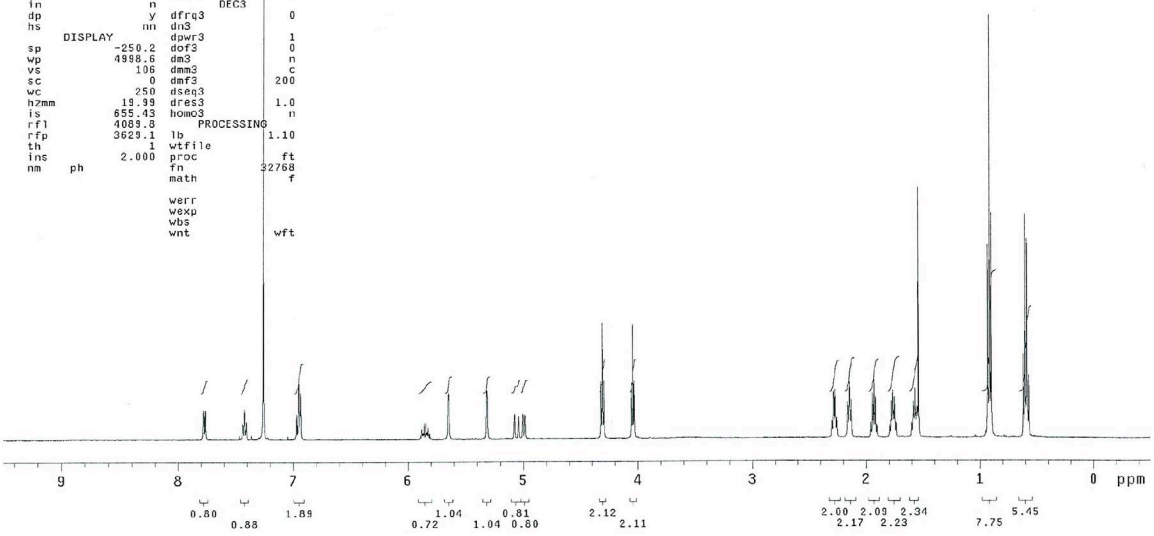
WYKELN5161_1H

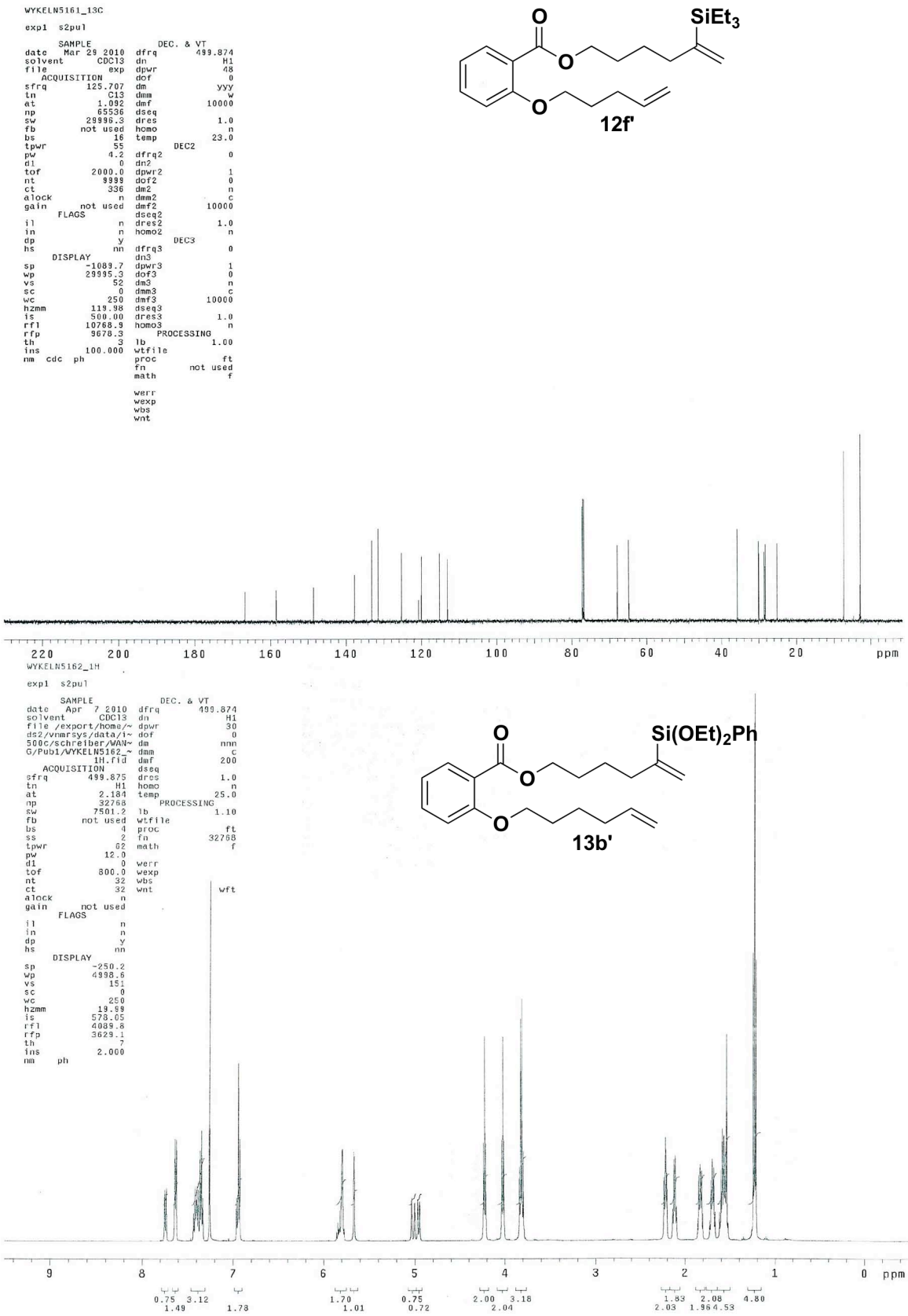
exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 29 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	23.0
ss	2	DEC2	
tpwr	52	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	32	dm2	n
ct	32	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	106	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	655.43	homo3	n
rfl	4089.8	PROCESSING	
rfp	3629.1	lb	1.10
th	1	wtfile	
ins	2.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft



12f'

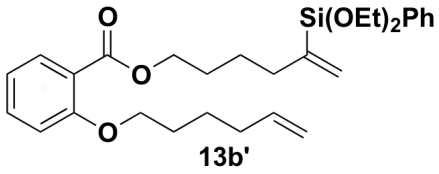



WYKELN5161_13C
expl s2pul
SAMPLE
date Mar 29 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 9999
ct 336
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1089.7
wp 29995.3
vs 52
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.9
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 23.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
SiEt3
O
O
12f'
220
200
180
160
140
120
100
80
60
40
20
ppm
WYKELN5162_1H
expl s2pul
SAMPLE
date Apr 7 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN5162_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 578.05
rfl 4089.8
rfp 3629.1
th 7
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
Si(OEt)2Ph
O
O
13b'
9
8
7
6
5
4
3
2
1
0 ppm
0.75 3.12
1.49 1.78
1.70
1.01
0.75
0.72
2.00 3.18
2.04
1.83 2.08 4.80
2.03 1.96 4.53

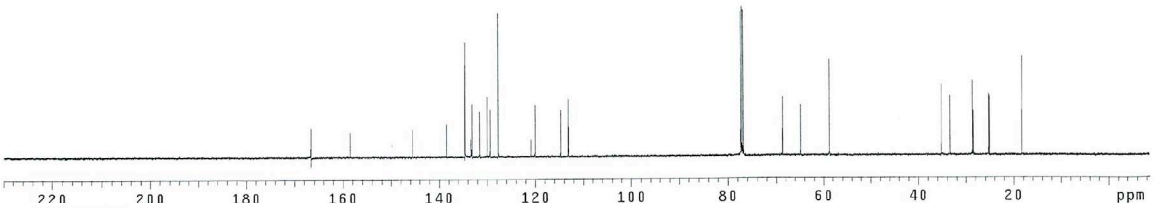
WYKELN5162_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 7 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1200	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1088.7	dpwr3	1
wp	29995.3	dof3	0
vs	33	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.0	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



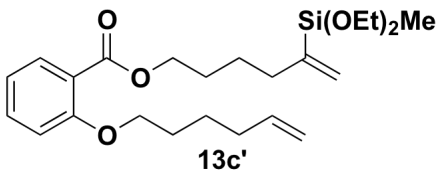
13b'



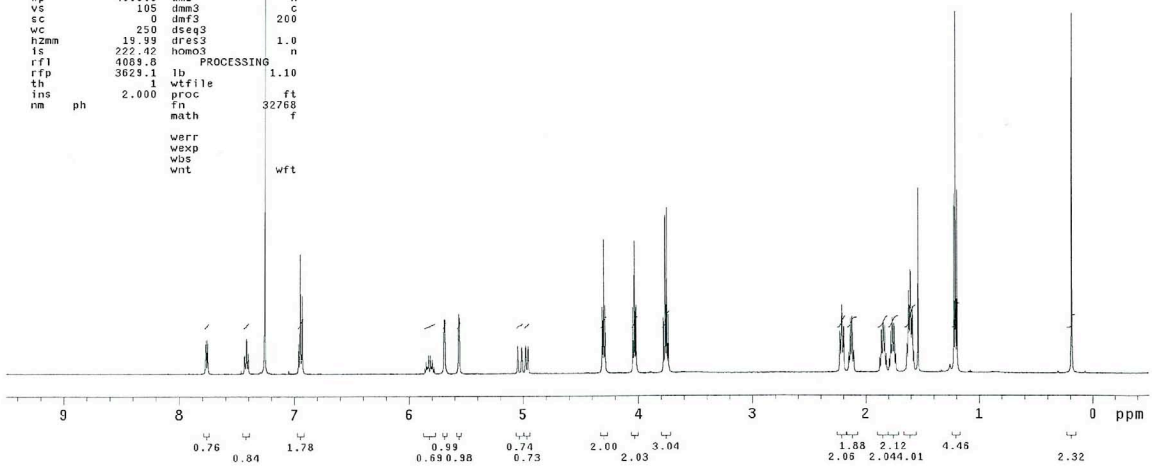
WYKELN5137_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 1 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	32	dm2	n
ct	0	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	105	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	222.42	homo3	n
rfl	4089.8	PROCESSING	
rfp	3629.1	lb	1.10
th	1	wtfile	
ins	2.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft



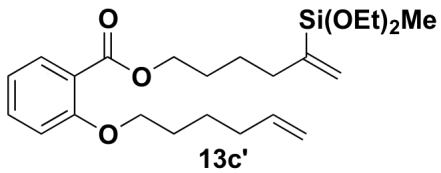
13c'



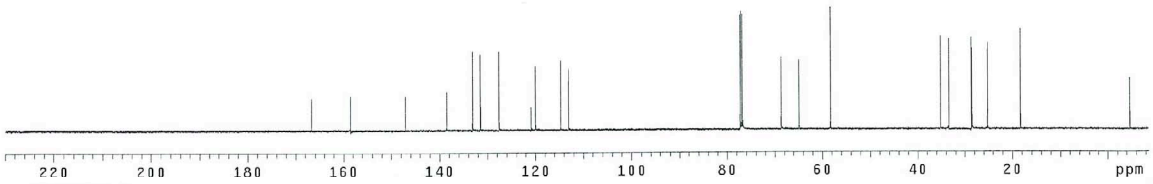
WYKELN5137_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 1 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	0	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1088.7	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.0	homo3	n
rfp	9678.3	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



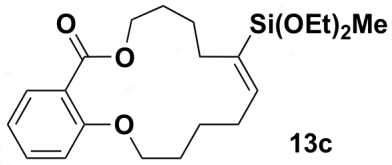
13c'



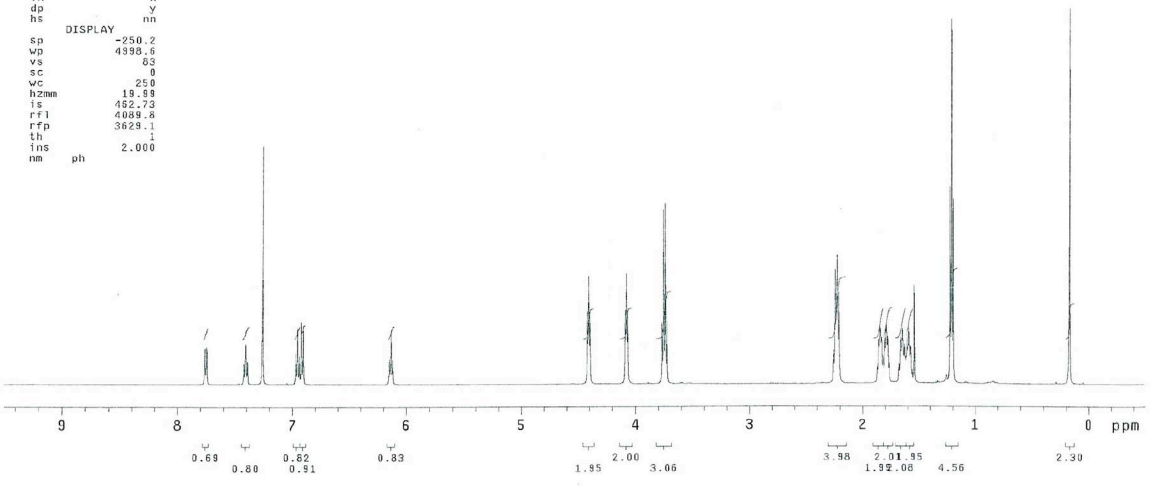
WYKELN10016_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 5 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/1~	dof	0
	500c/schreiber/WAN~	dm	nnn
	G/Pub1/WYKELN10016~	dmm	c
	1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	32	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	83		
sc	0		
wc	250		
hzmm	19.99		
is	462.73		
rfl	4089.8		
rfp	3629.1		
th	1		
ins	2.000		
nm ph			



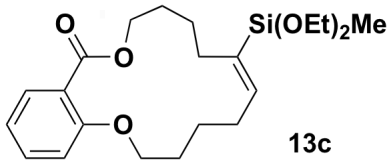
13c



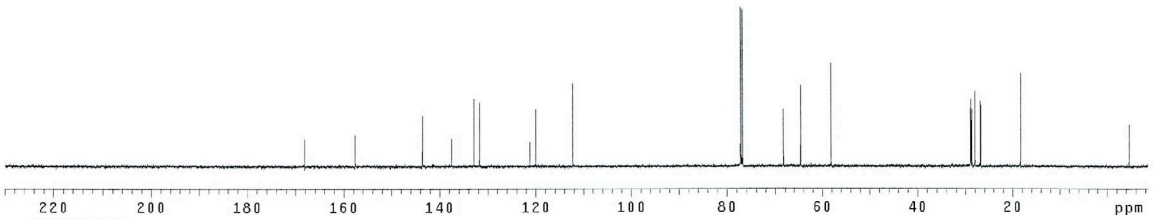
WYKELN10016_13C

exp4 s2pul

SAMPLE		DEC. & VT	
date	Apr 5 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	744	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1087.8	dpwr3	1
wp	29995.3	dof3	0
vs	35	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10767.1	homo3	n
rfp	9678.3	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



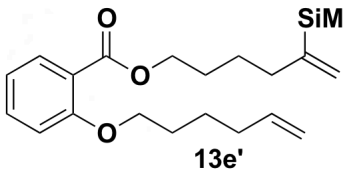
13c



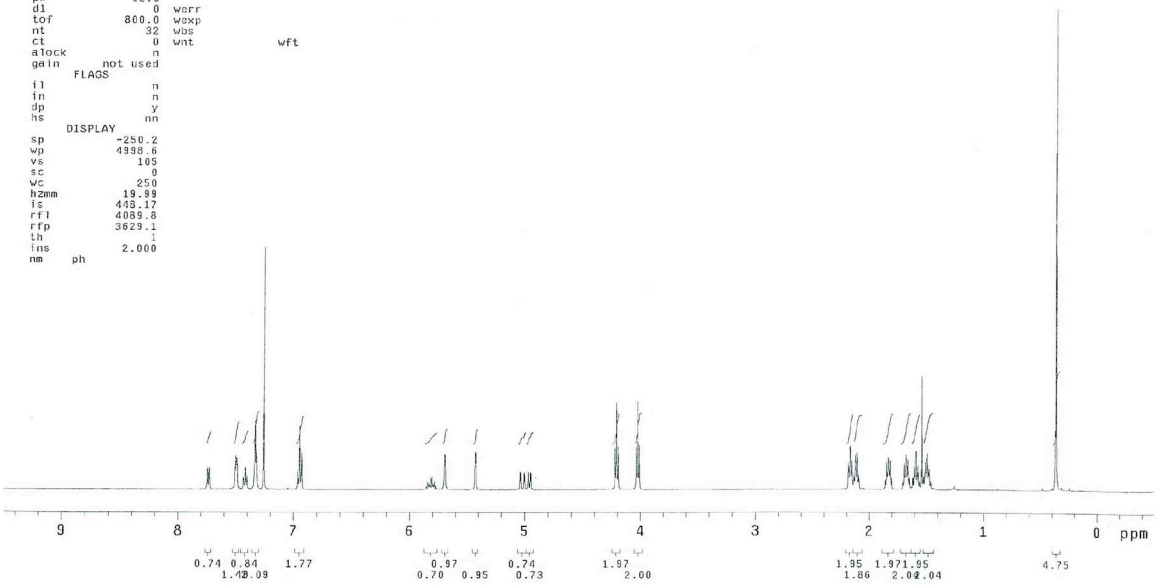
WYKELN5135_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 1 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/i~	dof	0
	500c/schreiber/WAN~	dm	nnn
	G/Pub1/WYKELN5135_~	dmm	c
	1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	52	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	0	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	105		
sc	0		
wc	250		
hzmm	19.99		
is	448.17		
rfl	4089.8		
rfp	3629.1		
th	1		
ins	2.000		
nm ph			



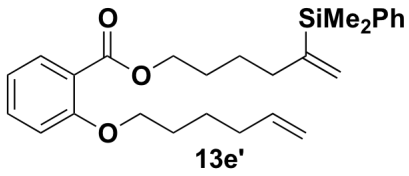
13e'



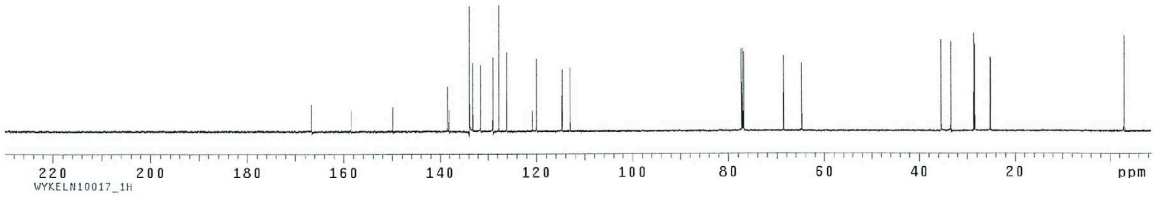
WYKELN5135_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 1 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29995.3	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	0	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1091.5	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10770.7	homo3	n
rfp	9678.3	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



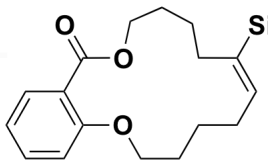
13e'



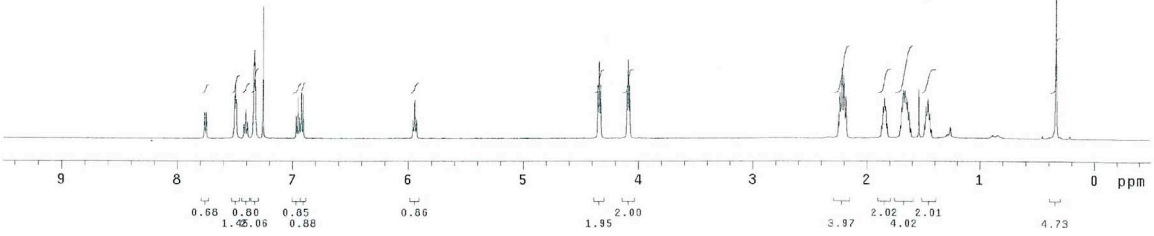
WYKELN10017_1H

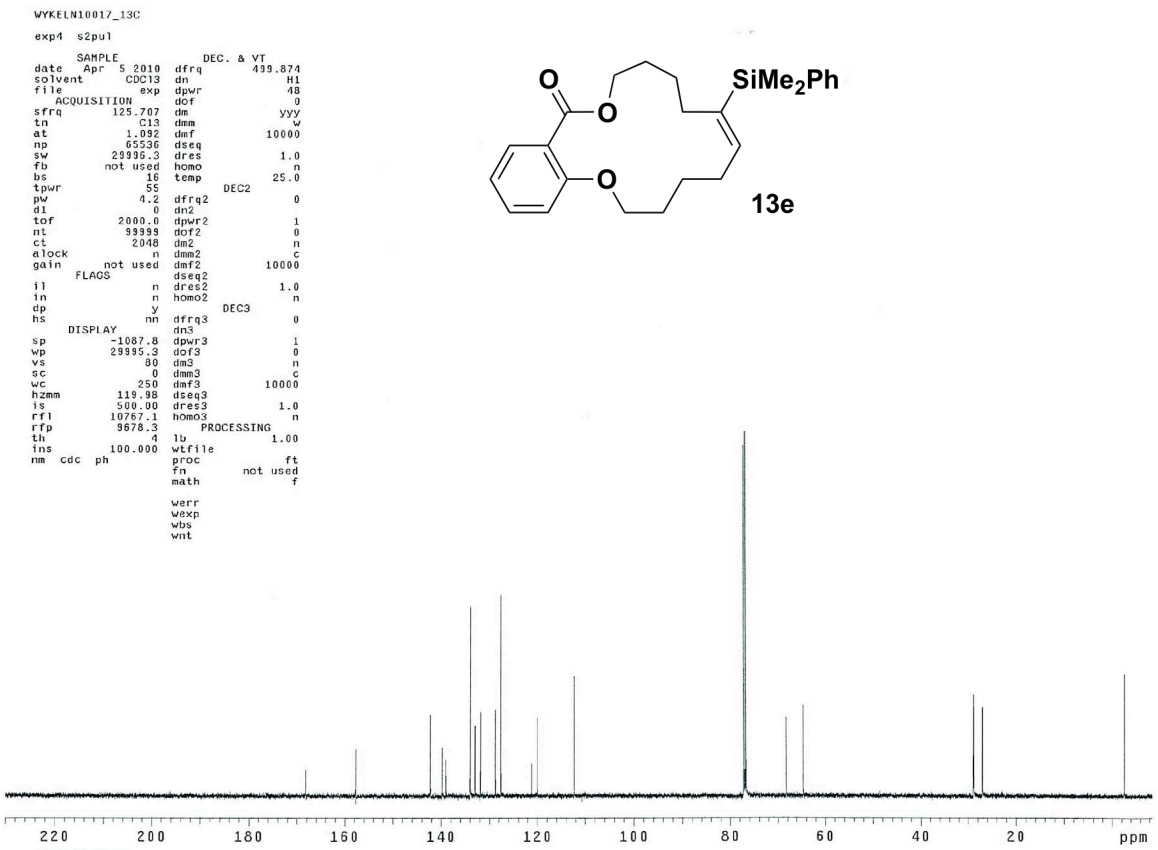
exp1 s2pul

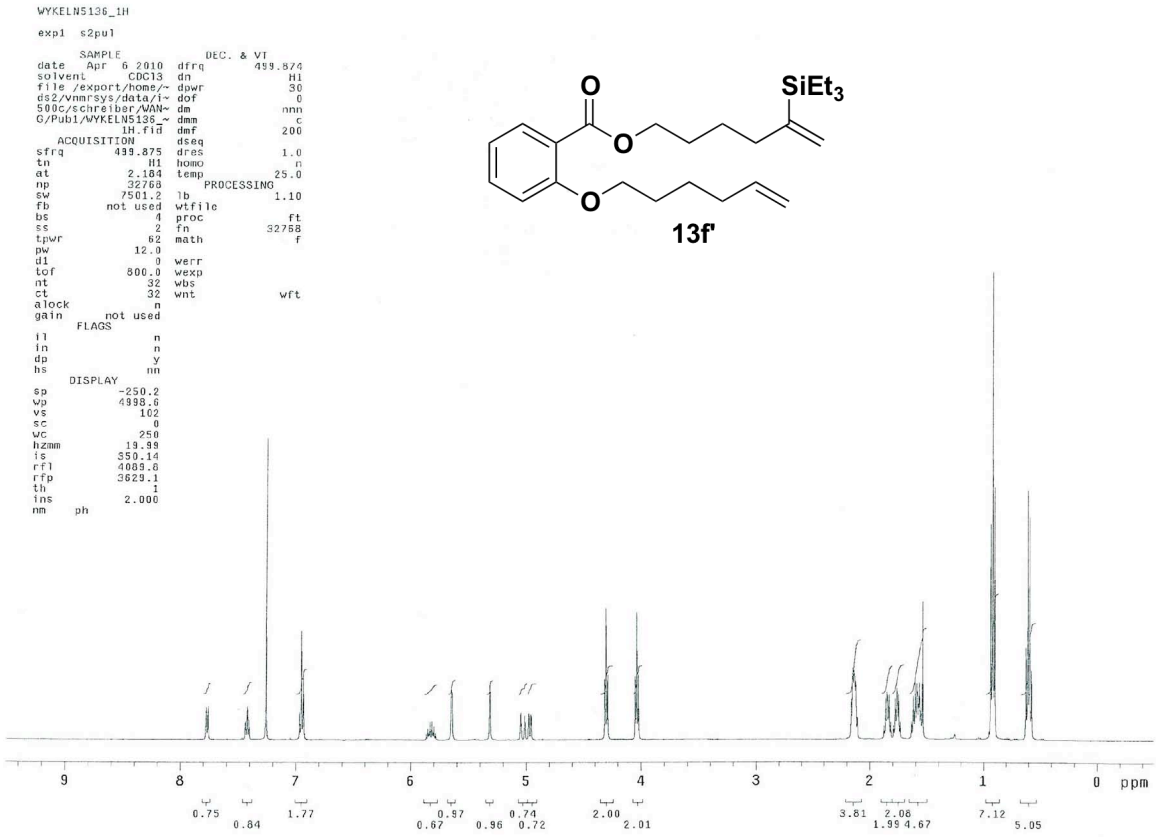
SAMPLE		DEC. & VT	
date	Apr 5 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/l~	dof	0
	500c/schreiber/WAN~	dm	nnn
	G/Pub1/WYKELN10017~	dmm	c
	_1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	32	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	125		
sc	0		
wc	250		
hzmm	19.98		
is	276.07		
rfl	4089.8		
rfp	3629.1		
th	1		
ins	2.000		
nm ph			

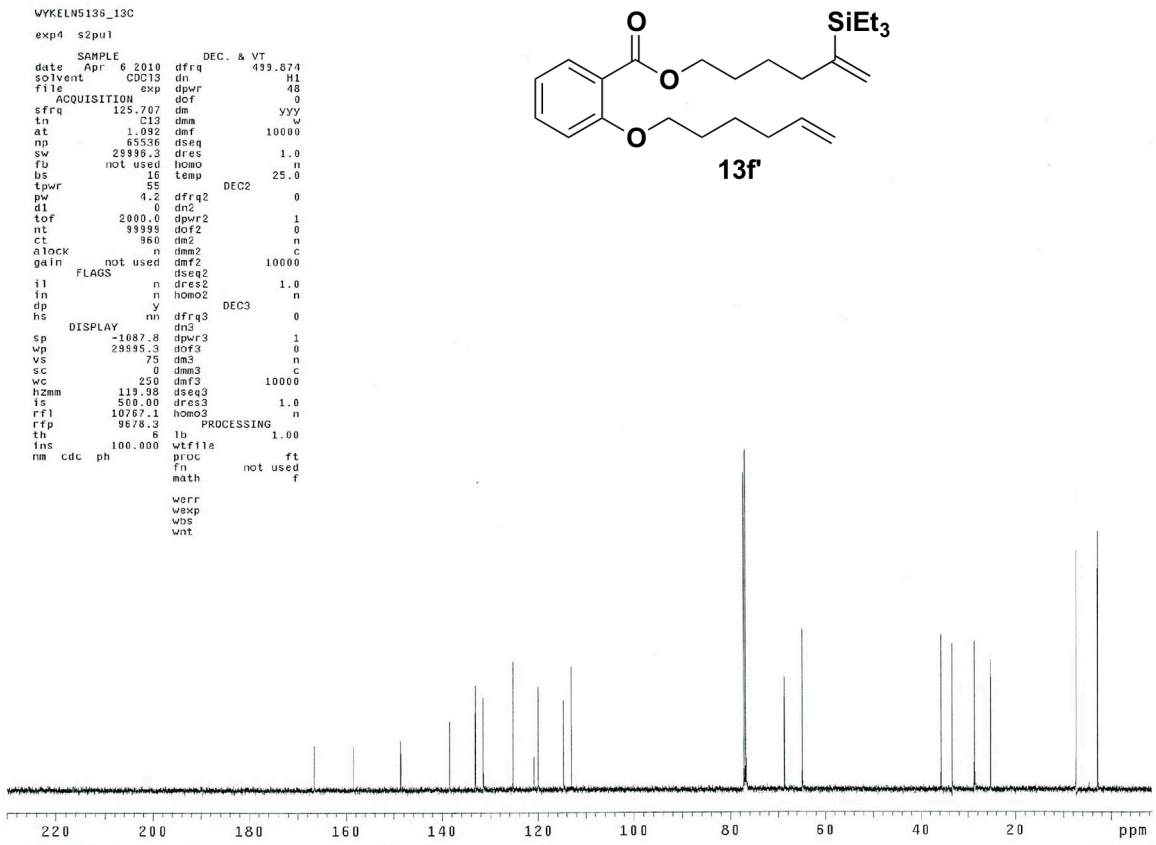


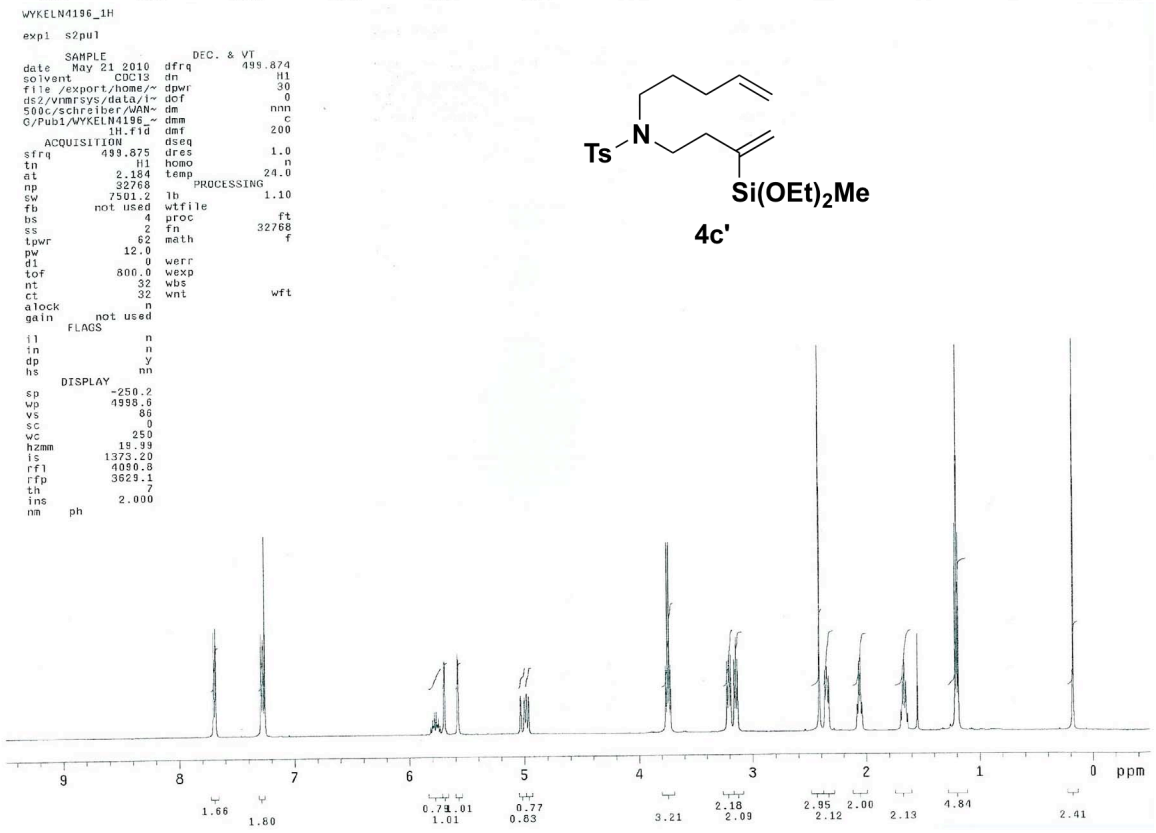
13e




WYKELN10017_13C
exp4 s2pul
SAMPLE
date Apr 5 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 2048
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 80
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
SiMe2Ph
13e
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN5136_1H
exp1 s2pul
SAMPLE
date Apr 6 2010
solvent CDCl3
file /export/home/~
ds2/Vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN5136_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 102
sc 0
wc 250
hzmm 19.99
is 350.14
rfl 4089.6
rfp 3629.1
th 1
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
SiEt3
13f'
9
8
7
6
5
4
3
2
1
0
ppm
0.75
0.84
1.77
0.87
0.67
0.96
0.74
0.72
2.00
2.01
3.81
2.08
1.99
4.67
7.12
5.05

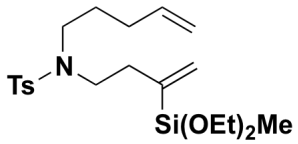

WYKELN5136_13C
exp4 s2pul
SAMPLE
date Apr 6 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 960
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 75
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 6
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
SiEt3
13f'
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN4196_1H
exp1 s2pul
SAMPLE
date May 21 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500c/schreiber/WAN~
G/Pub1/WYKELN4196_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 86
sc 0
wc 250
hzmm 19.99
is 1373.20
rfl 4090.8
rfp 3629.1
th 7
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 24.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
Ts
N
Si(OEt)2Me
4c'
9
8
7
6
5
4
3
2
1
0
ppm
1.66
1.80
0.79
1.01
1.01
0.77
0.83
3.21
2.18
2.09
2.95
2.12
2.00
2.13
4.84
2.41

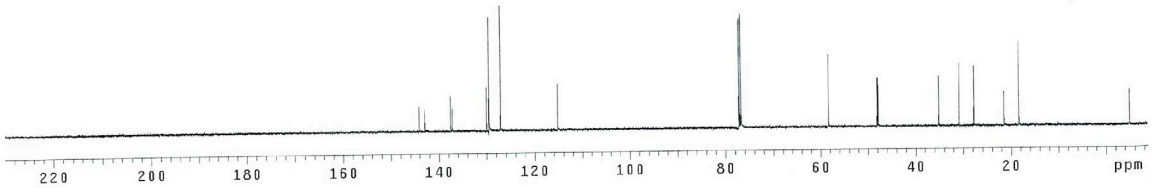
WYKELN4196_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	May 21 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	24.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	704	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1089.7	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.9	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



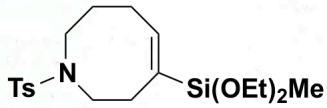
4c'



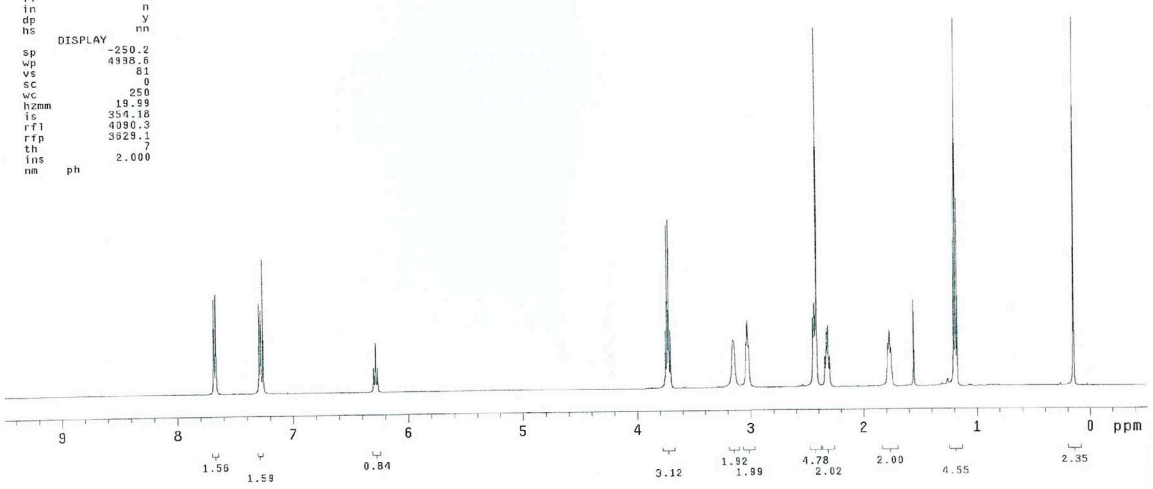
WYKELN10034_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 22 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
ds2/vnmrsys/data/1~		dof	0
500c/schreiber/WAN~		dm	nnn
G/Pub1/WYKELN10034~		dmm	c
1H.fid		dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	24.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0	werr	
d1	0	wexp	
tof	800.0	wbs	
nt	32	wnt	wft
ct	32		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	81		
sc	0		
wc	250		
hzmm	19.99		
is	354.18		
rfl	4090.3		
rfp	3629.1		
th	7		
ins	2.000		
nm ph			



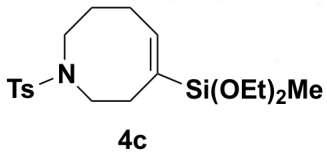
4c



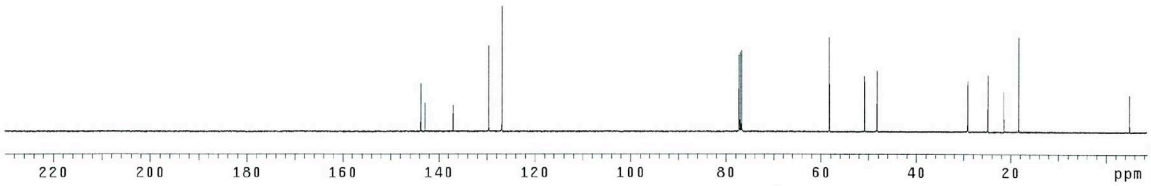
WYKELN10034_13C

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 22 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29986.3	dres	1.0
fb	not used	homo	n
bs	32	temp	24.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1248	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1090.6	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10769.8	homo3	n
rfp	9678.3	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



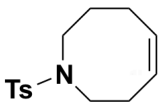
4c



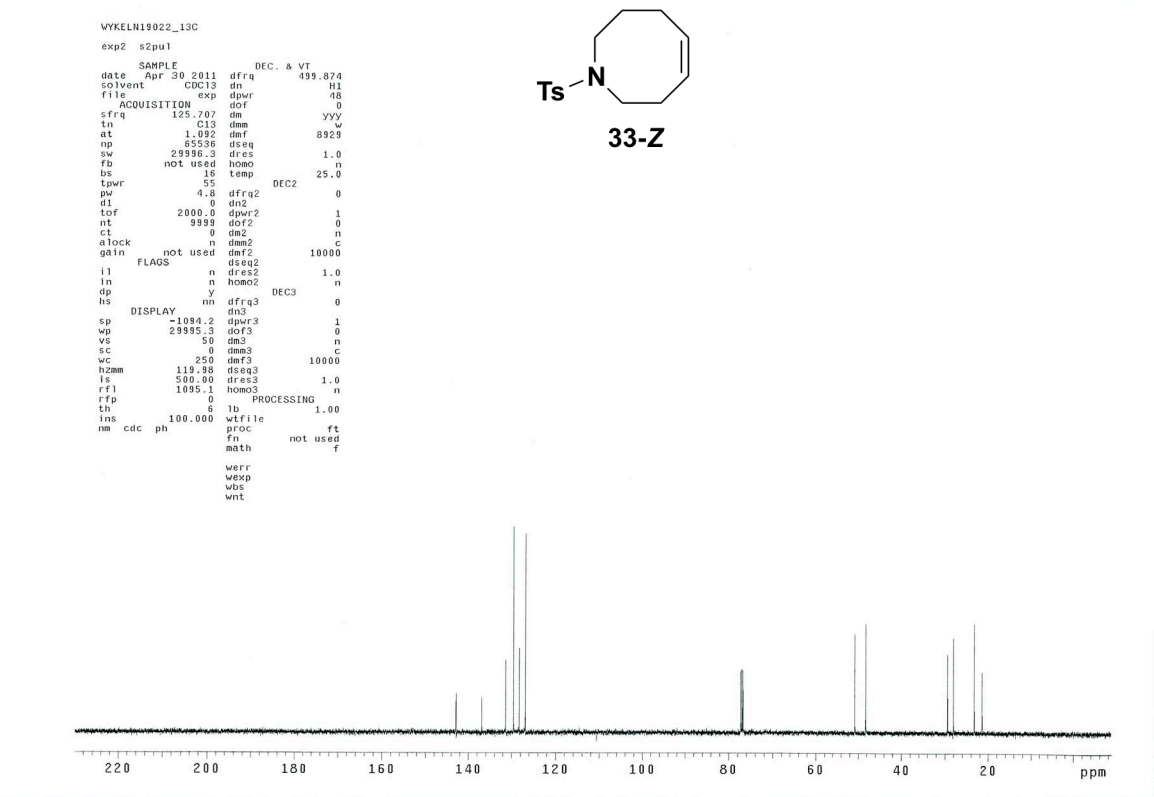
WYKELN19022_1H

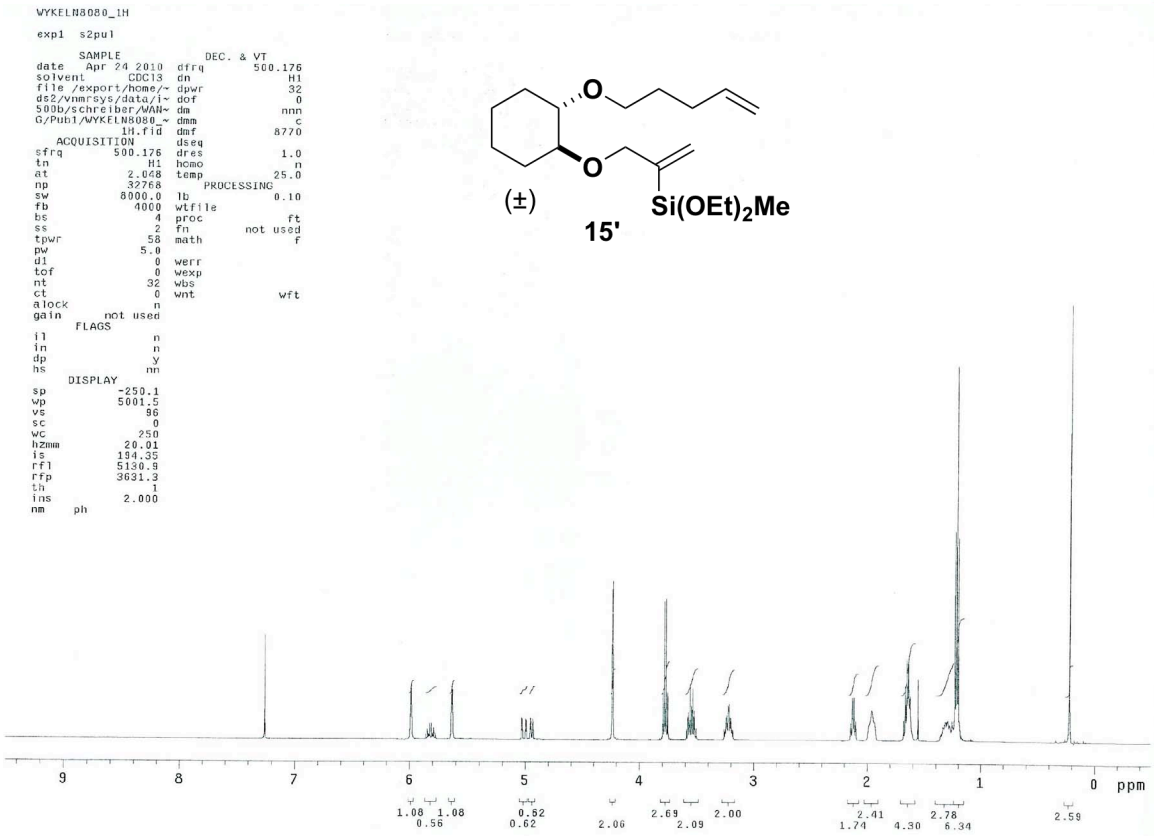
exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	16	dm2	n
ct	0	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	151	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	423.92	homo3	n
rfl	460.3	PROCESSING	
rfp	0	lb	1.10
th	2	wtfile	
ins	2.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft



33-*Z*

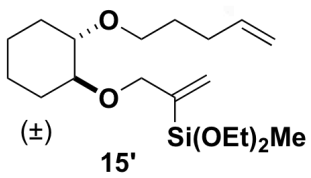

WYKELN19022_13C
exp2 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1094.2
wp 29995.3
vs 50
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 1095.1
rfp 0
th 6
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Ts
N
33-Z
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN8080_1H
exp1 s2pul
SAMPLE
date Apr 24 2010
solvent CDCl3
file /export/home/~ dpwr 32
ds2/vnmrsys/data/i~ dof 0
500b/schreiber/WAN~ dm nnn
G/Pub1/WYKELN8080_~ dmm c
1H.fid dmf 8770
ACQUISITION dseq
sfrq 500.176 dres 1.0
tn H1 homo n
at 2.048 temp 25.0
np 32768 PROCESSING
sw 8000.0 lb 0.10
fb 4000 wtfile
bs 4 proc ft
ss 2 fn not used
tpwr 58 math f
pw 5.0
d1 0 werr
tof 0 wexp
nt 32 wbs
ct 0 wnt wft
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 96
sc 0
wc 250
hzmm 20.01
is 194.35
rfl 5130.8
rfp 3631.3
th 1
ins 2.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
O
O
(±)
Si(OEt)2Me
15'
9
8
7
6
5
4
3
2
1
0 ppm
1.08 1.08
0.56
0.62
0.62
2.06
2.69
2.09
2.00
2.41
1.74
4.30
2.78
6.34
2.59

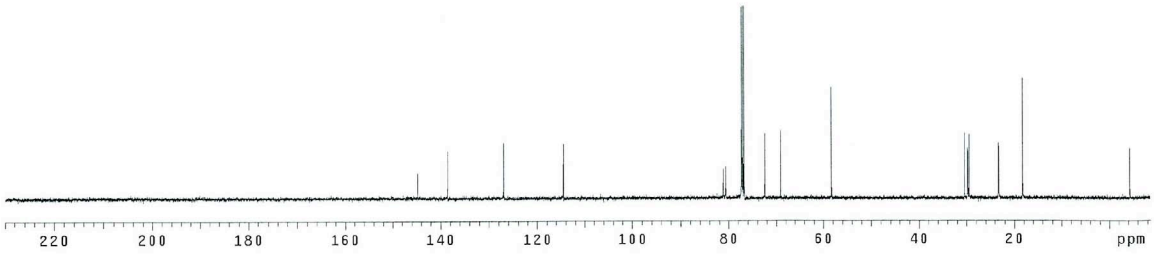
WYKELN8080_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 25 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	2.0	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	848	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1088.7	dpwr3	1
wp	29995.3	dof3	0
vs	42	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.0	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



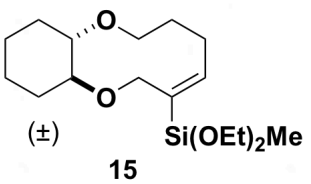
15'



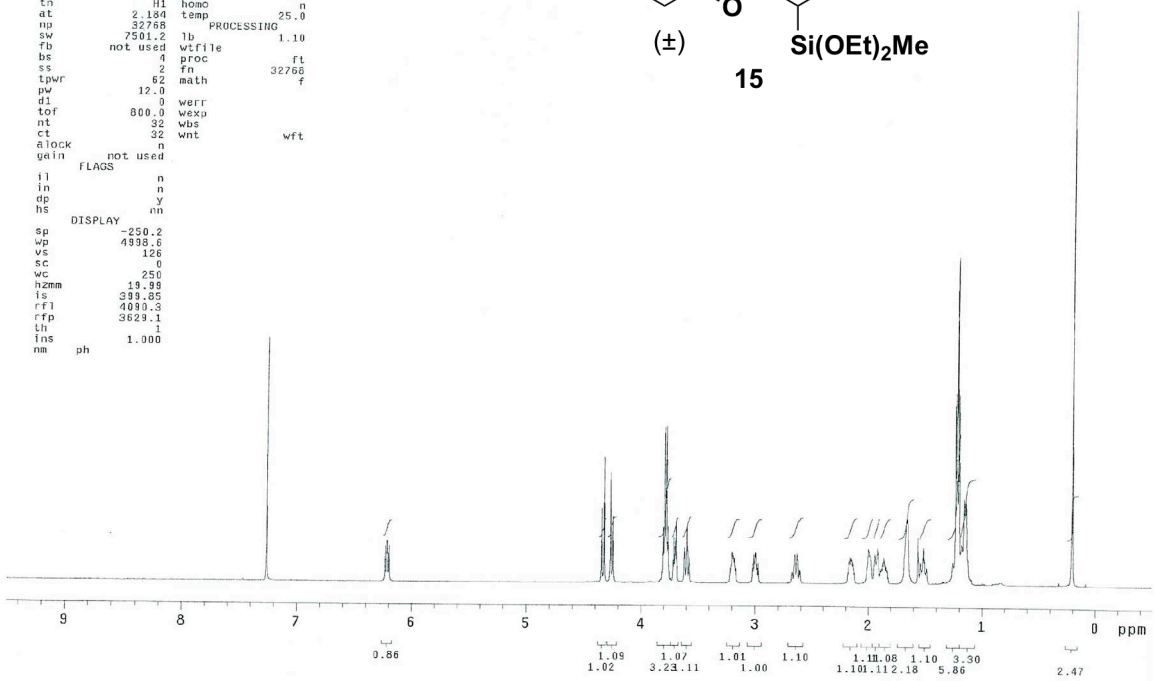
WYKELN10023_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 26 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
ds2/vnmrsys/data/i~		dof	0
500c/schreiber/WAN~		dm	nnn
G/Pub1/WYKELN10023~		dmm	c
	_1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0	werr	
d1	0	wexp	
tof	800.0	wbs	
nt	32	wnt	wft
ct	32		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	126		
sc	0		
wc	250		
hzmm	19.98		
is	399.85		
rfl	4090.3		
rfp	3629.1		
th	1		
ins	1.000		
nm ph			



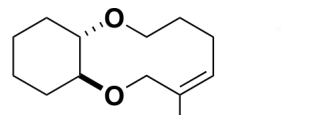
15



WYKELN10023_13C

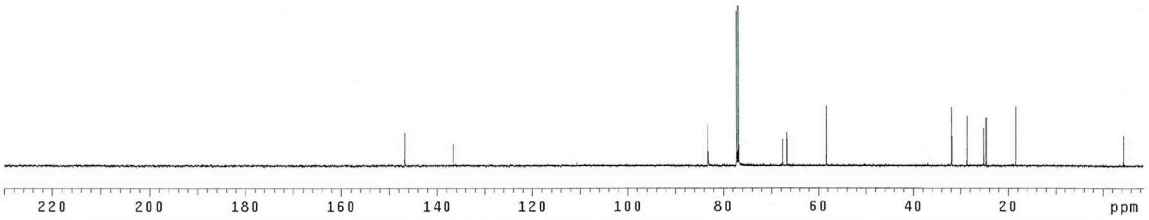
exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 26 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1248	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1086.9	dpwr3	1
wp	29995.3	dof3	0
vs	35	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10766.2	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



(±) $Si(OEt)_2Me$

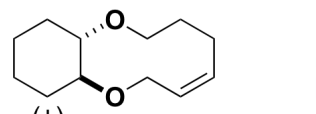
15



WYKELN19023_1H

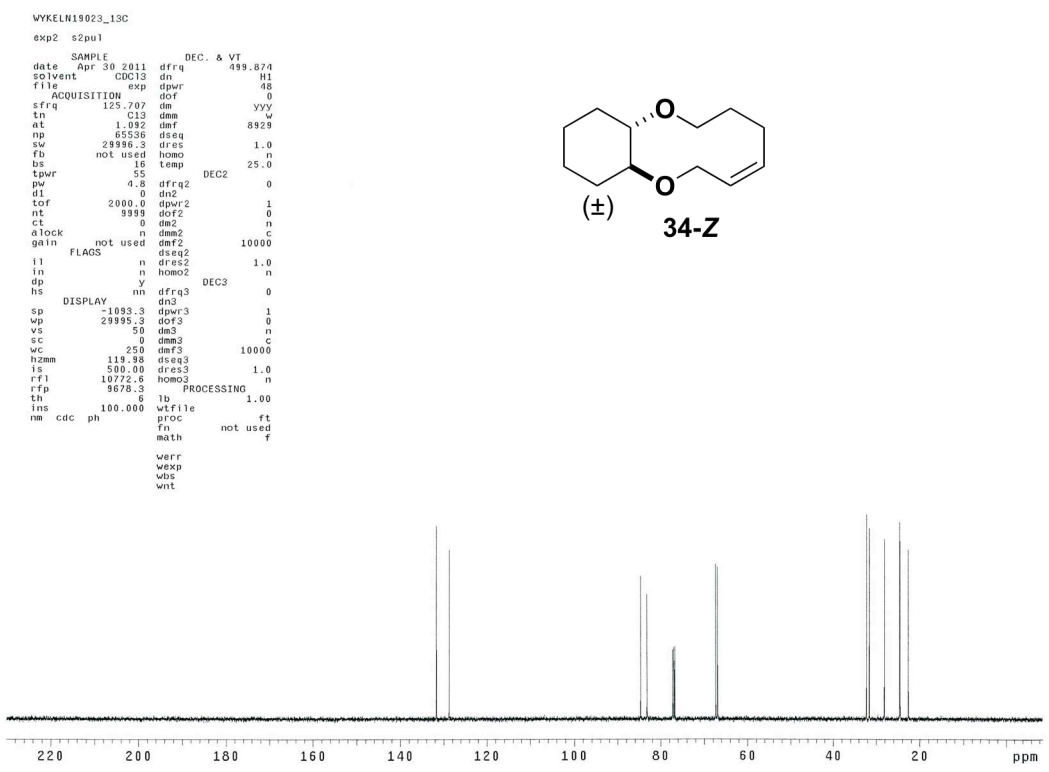
exp1 s2pul

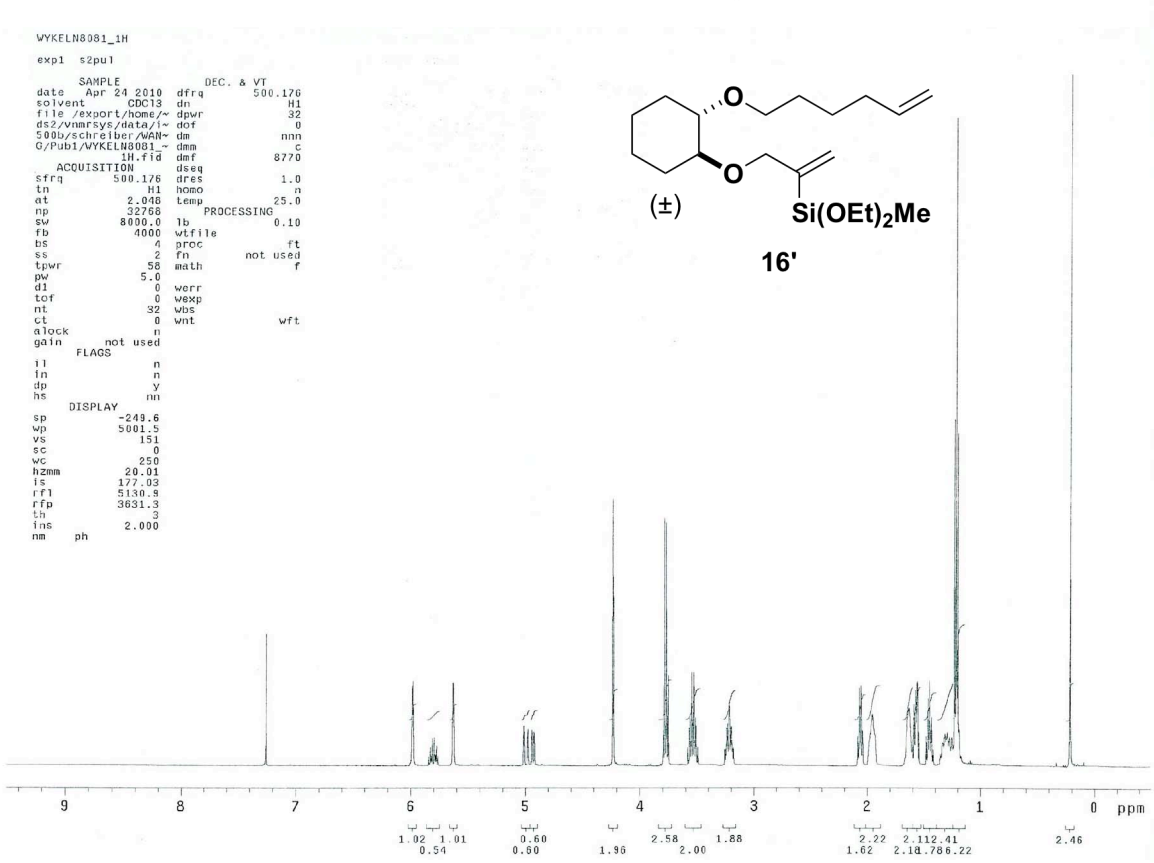
SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	16	dm2	n
ct	0	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	151	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	204.99	homo3	n
rfl	4089.8	PROCESSING	
rfp	3629.1	lb	1.10
th	3	wtfile	
ins	1.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft

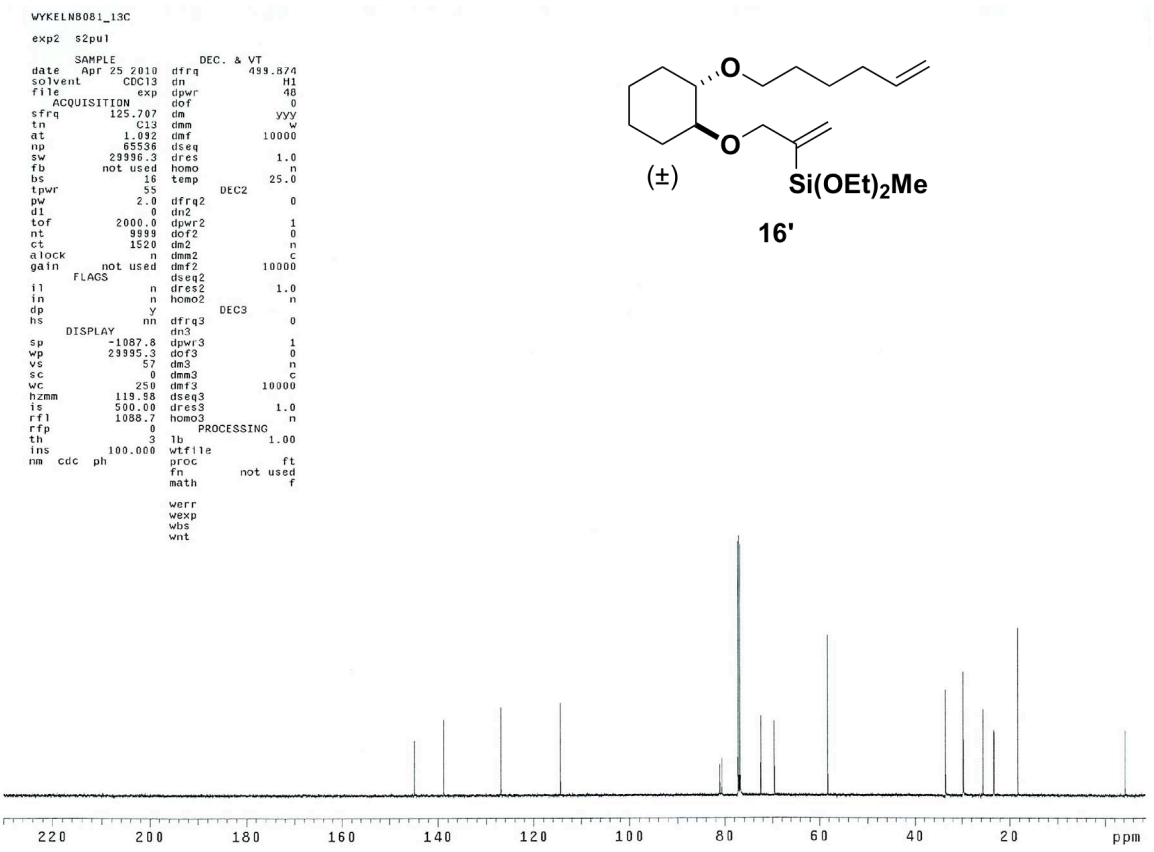


(±)

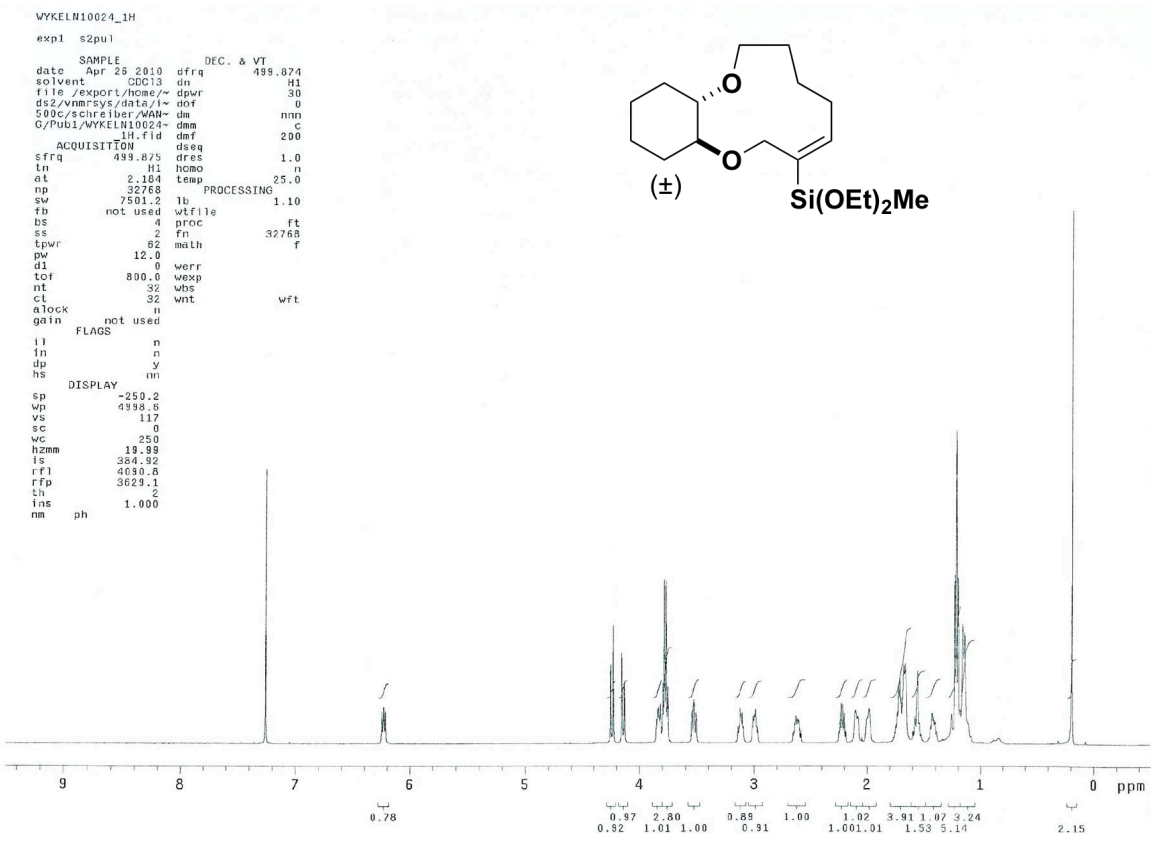
34-*Z*


WYKELN19023_13C
exp2 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1093.3
wp 29995.3
vs 50
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10772.6
rfp 9678.3
th 6
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
(±)
34-Z
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN8081_1H
exp1 s2pul
SAMPLE
date Apr 24 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/l~
500b/schreiber/WAN~
G/Pub1/WYKELN8081_~
1H.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -249.6
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 177.03
rfl 5130.8
rfp 3631.3
th 3
ins 2.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
(±)
Si(OEt)2Me
16'
9
8
7
6
5
4
3
2
1
0
ppm
1.02 1.01
0.54
0.60
0.60
1.96
2.58
2.00
1.88
2.22
1.62
2.11
2.18
2.41
1.78
6.22
2.46


WYKELN8081_13C
exp2 s2pul
SAMPLE
date Apr 25 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 2.0
d1 0
tof 2000.0
nt 9999
ct 1520
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 57
sc 0
wc 250
hzmm 119.58
is 500.00
rfl 1088.7
rfp 0
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
(±)
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

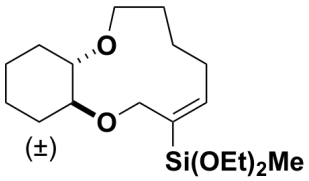
16'

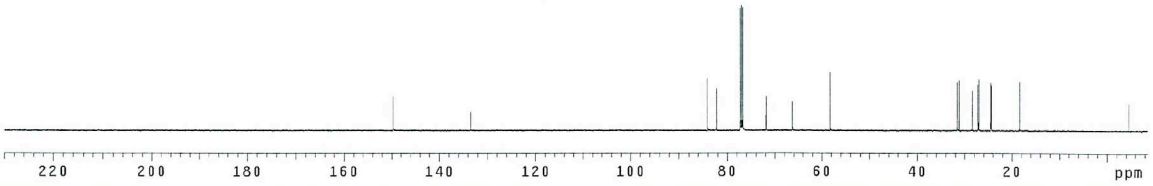

WYKELN10024_1H
exp1 s2pul
SAMPLE
date Apr 25 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/l~
500c/schreiber/WAN~
G/Publ/WYKELN10024~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.5
vs 117
sc 0
wc 250
hzmm 19.99
is 384.92
rfl 4010.6
rfp 3629.1
th 2
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
(±)
Si(OEt)2Me
9
8
7
6
5
4
3
2
1
0 ppm
0.78
0.97
0.92
2.80
1.01 1.00
0.89
0.91
1.00
1.02
1.001.01
3.91 1.07 3.24
1.53 5.14
2.15

WYKELN10024_13C

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 26 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1792	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1086.9	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.58	dseq3	
is	500.00	dres3	1.0
rfl	10766.2	homo3	n
rfp	9678.3	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	

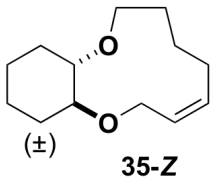


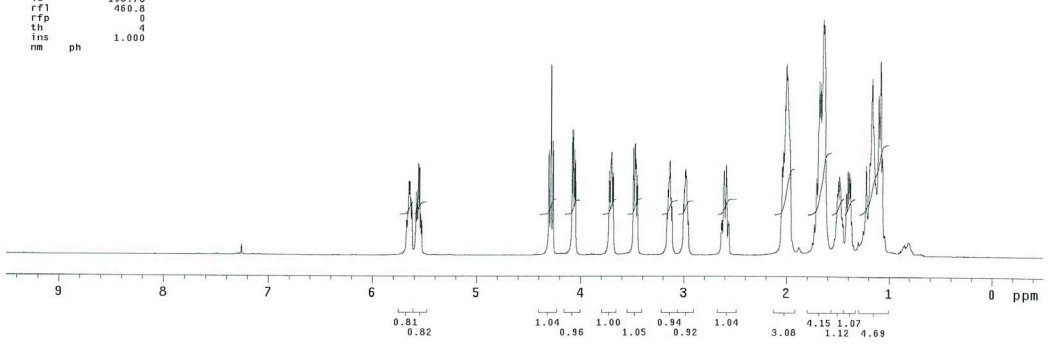


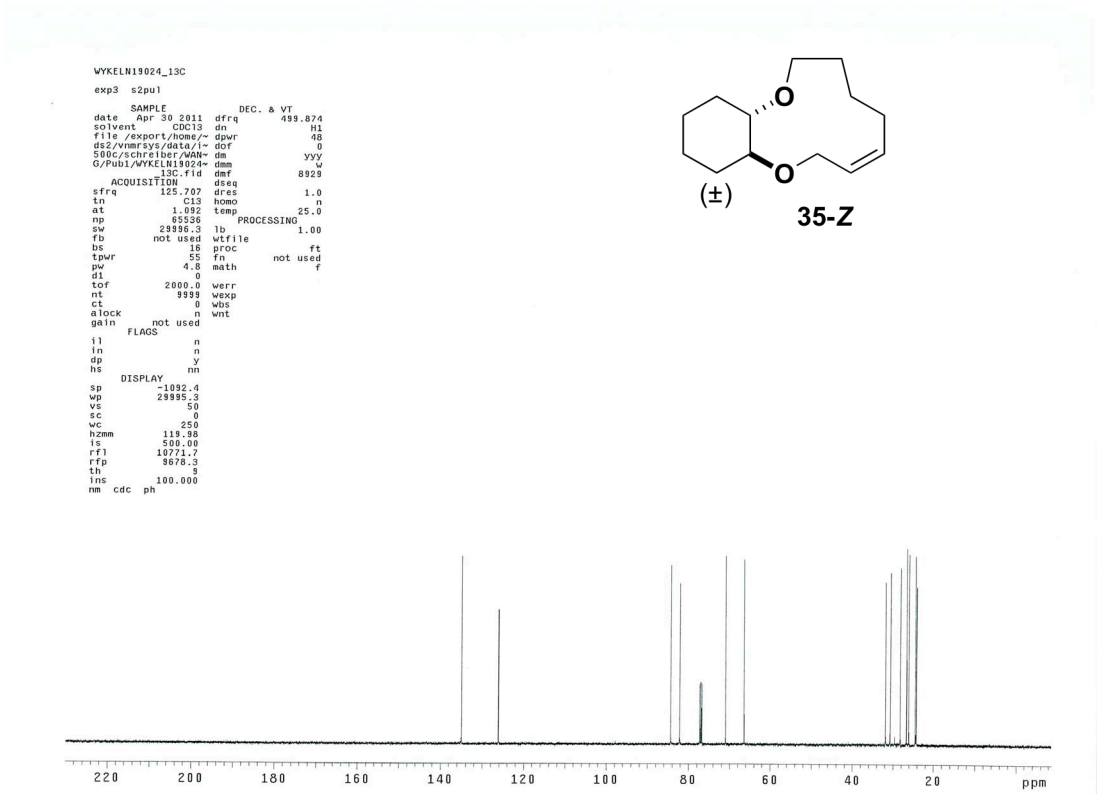
WYKELN19024_1H

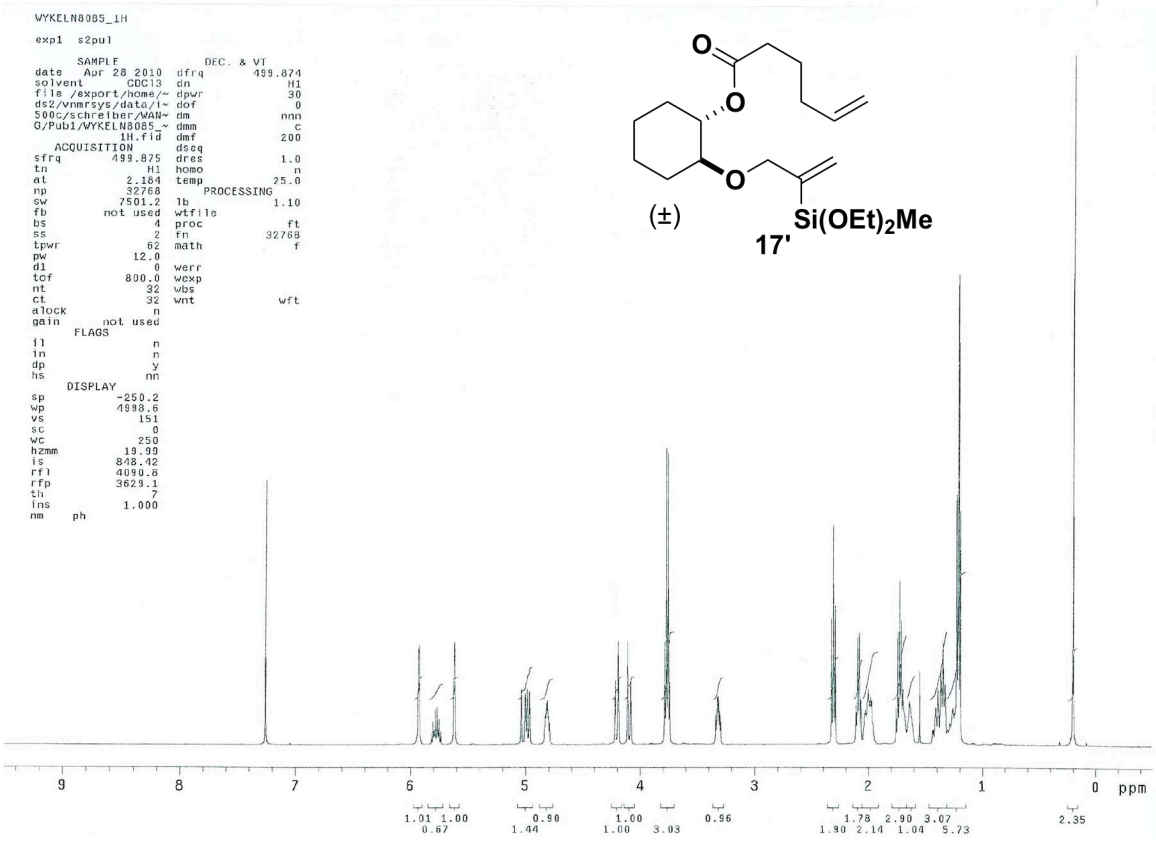
exp3 s2pul

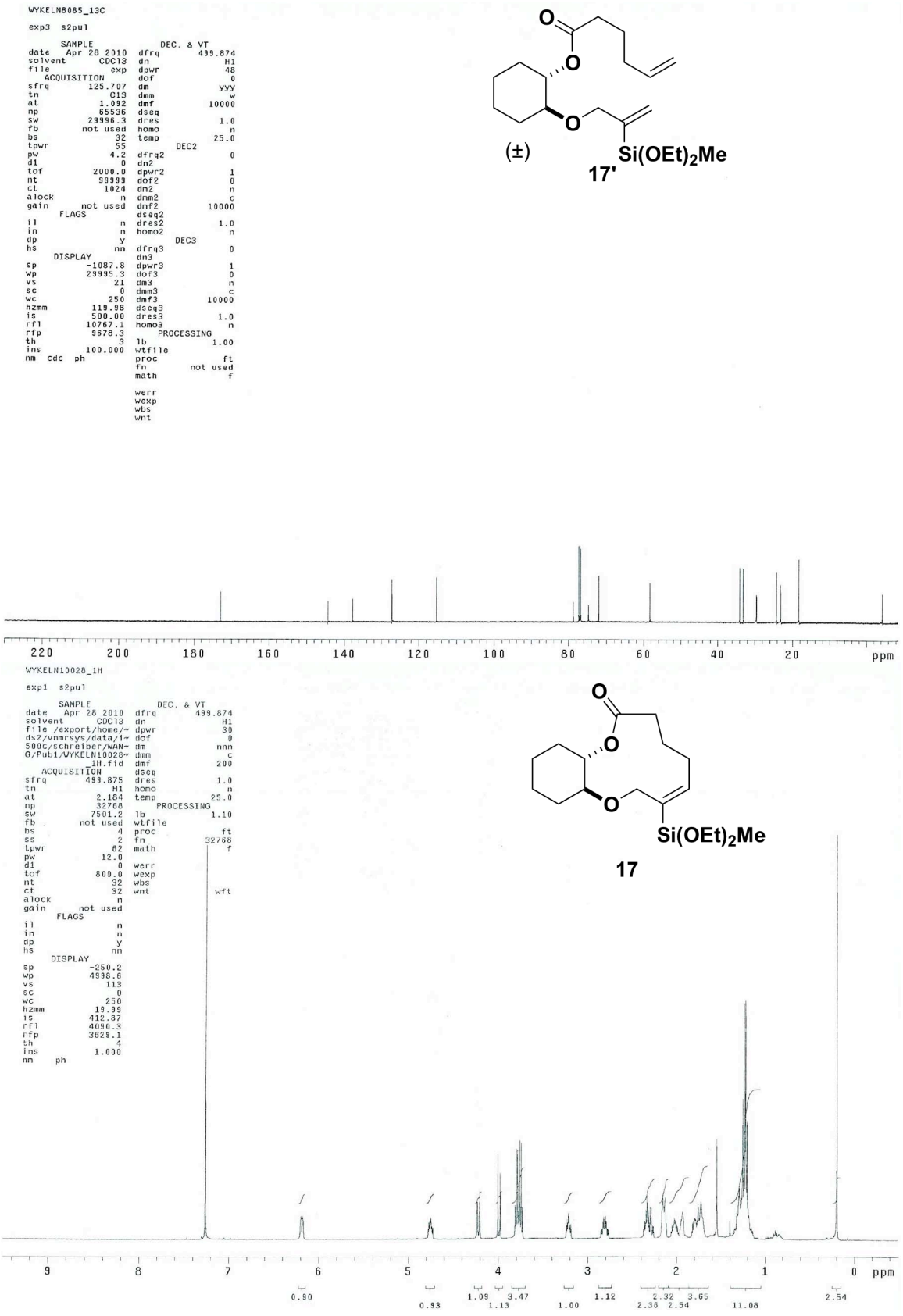
SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
ds2/vnmrsys/data/i~		dof	0
500c/schreiber/WAN~		dm	nnn
G/Pub1/WYKELN19024~		dmm	c
1H.fid		dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	16	wbs	
ct	0	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	57		
sc	0		
wc	250		
hzmm	19.99		
is	198.78		
rfl	460.8		
rfp	0		
th	4		
ins	1.000		
nm ph			






WYKELN19024_13C
exp3 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/~
500c/schreiber/WAN~
G/Pub1/WYKELN19024~
13C.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1092.4
wp 29985.3
vs 50
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10771.7
rfp 9678.3
th 9
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
(±)
35-Z
220
200
180
160
140
120
100
80
60
40
20
ppm

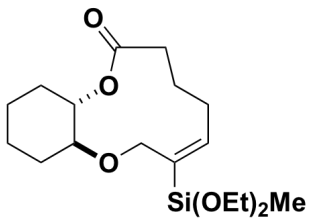

WYKELN8085_1H
exp1 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/~
500c/schreiber/WAN~
G/Pub1/WYKELN8085_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 848.42
rfl 4090.8
rfp 3629.1
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
(±)
Si(OEt)2Me
17'
9
8
7
6
5
4
3
2
1
0
ppm
1.01 1.00
0.67
0.90
1.44
1.00
1.00
3.03
0.96
1.78 2.90 3.07
1.90 2.14 1.04 5.73
2.35


WYKELN8085_13C
exp3 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 1024
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 21
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
Si(OEt)2Me
17'
220
200
180
160
140
120
100
80
60
40
20
ppm
WYKELN10028_1H
exp1 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN10028~
_1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 113
sc 0
wc 250
hzmm 19.98
is 412.87
rfl 4090.3
rfp 3629.1
th 4
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
17
9
8
7
6
5
4
3
2
1
0
ppm
0.90
0.93
1.09
3.47
1.13
1.00
1.12
2.32
3.65
2.36
2.54
11.08
2.54

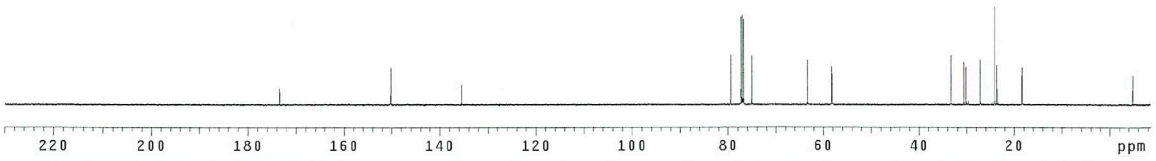
WYKELN10028_13C

exp3 s2pul

SAMPLE		DEC. & VT	
date	Apr 28 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1088	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1087.8	dpwr3	1
wp	29995.3	dof3	0
vs	21	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10767.1	homo3	n
rfp	9678.3	PROCESSING	
th	5	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



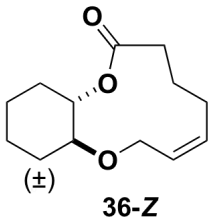
17



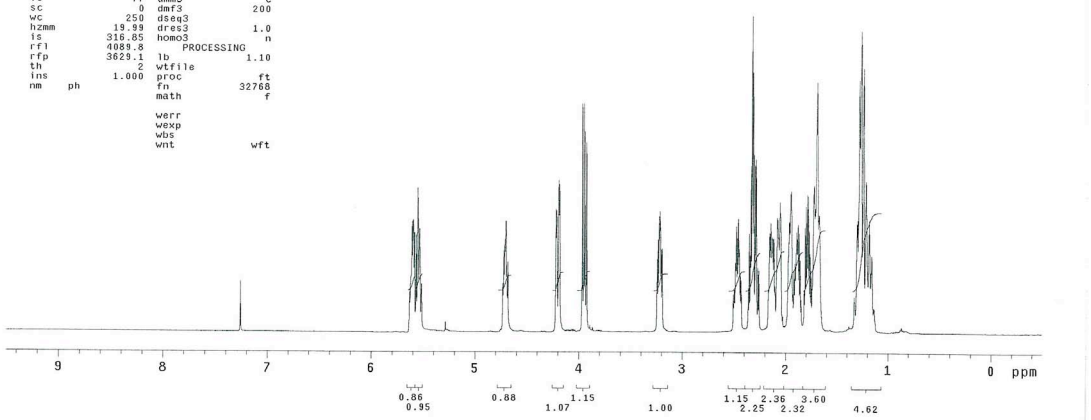
WYKELN19028_1H

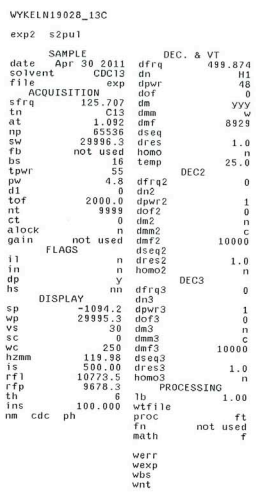
exp1 s2pul

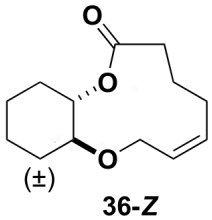
SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	16	dm2	n
ct	0	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	77	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	316.85	homo3	n
rfl	4089.8	PROCESSING	
rfp	3629.1	lb	1.10
th	2	wtfile	
ins	1.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft



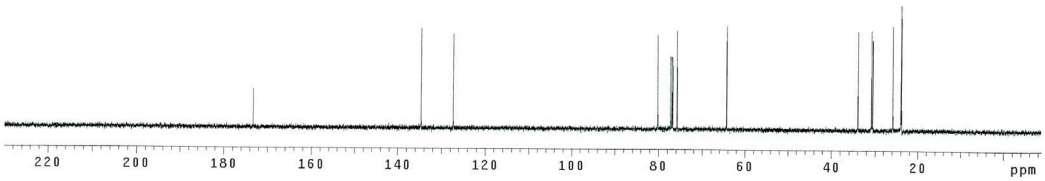
36-*Z*

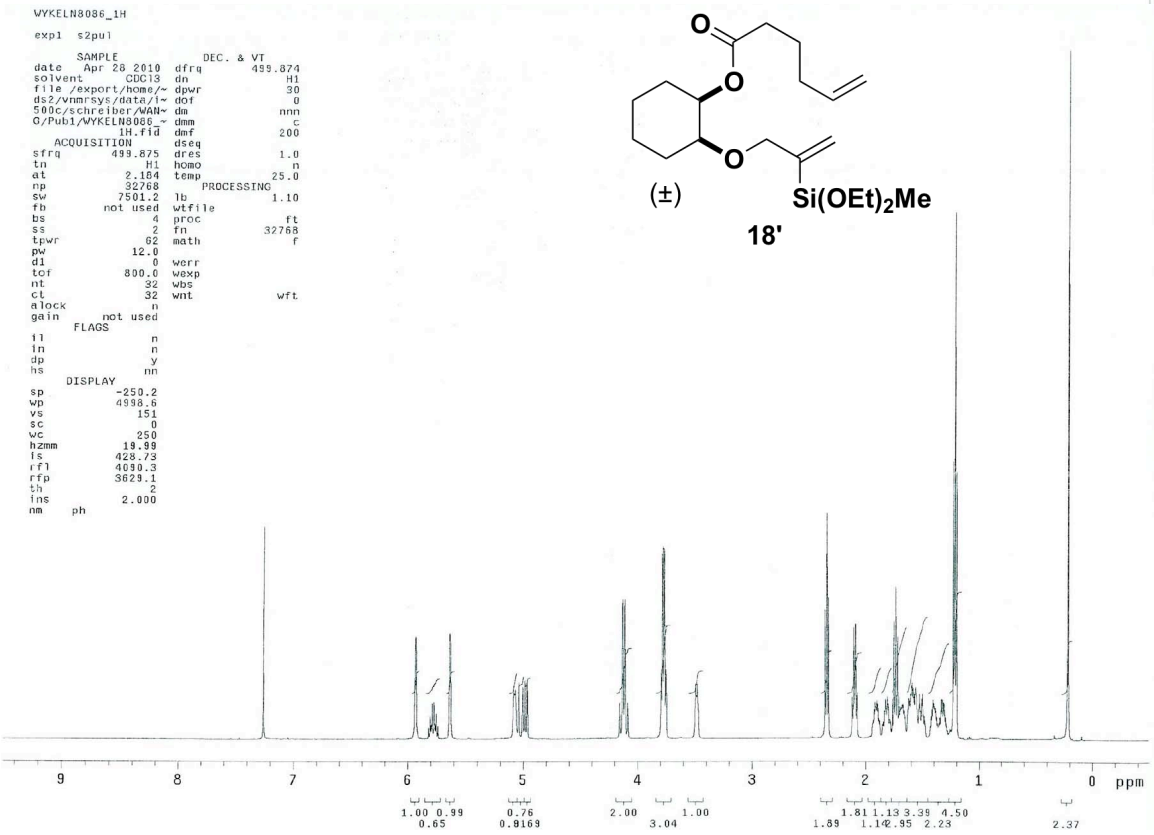



WYKELN19028_13C
exp2 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1094.2
wp 29995.3
vs 30
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10773.5
rfp 9678.3
th 6
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt


O
O
O
(±)

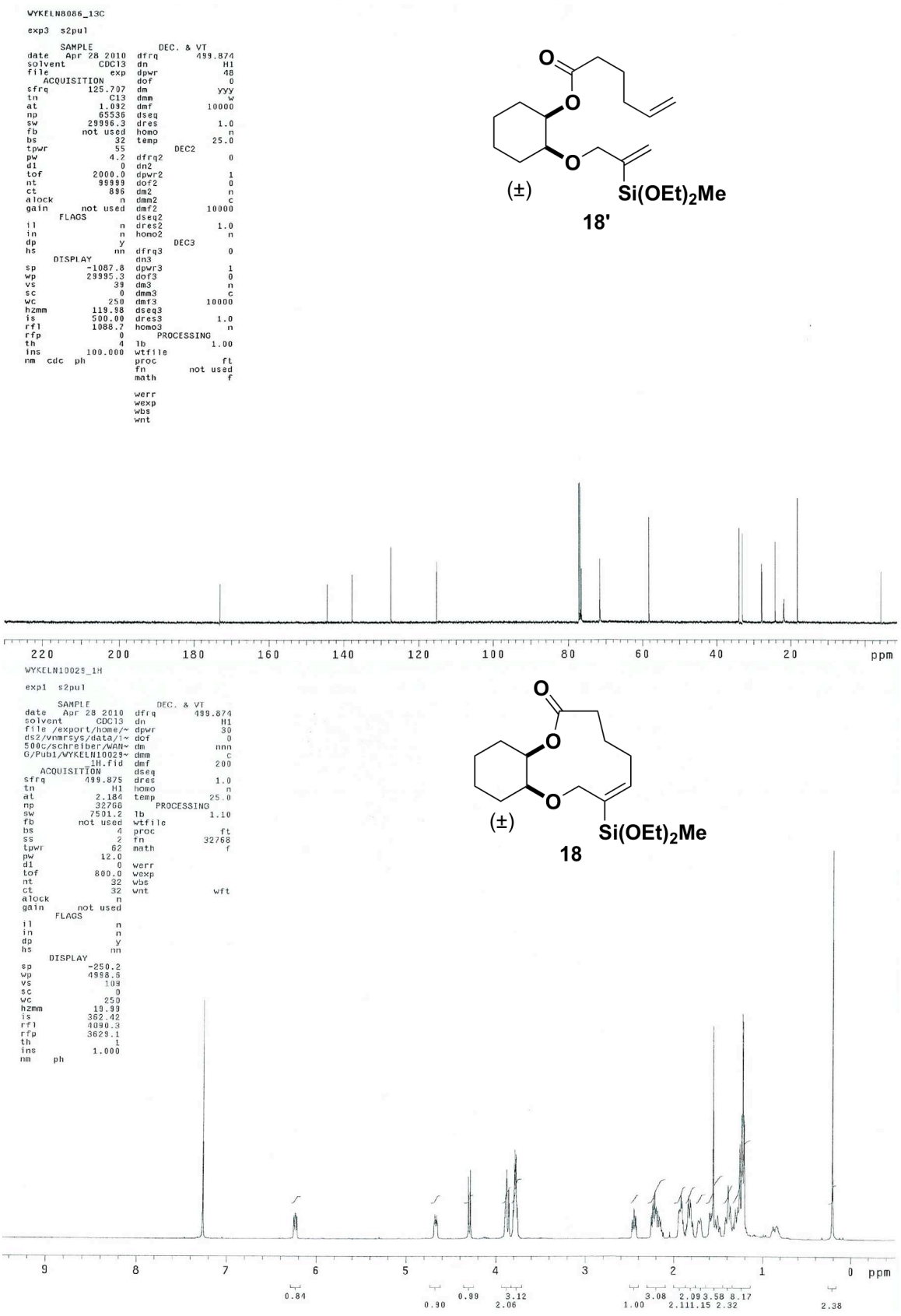
36-*Z*

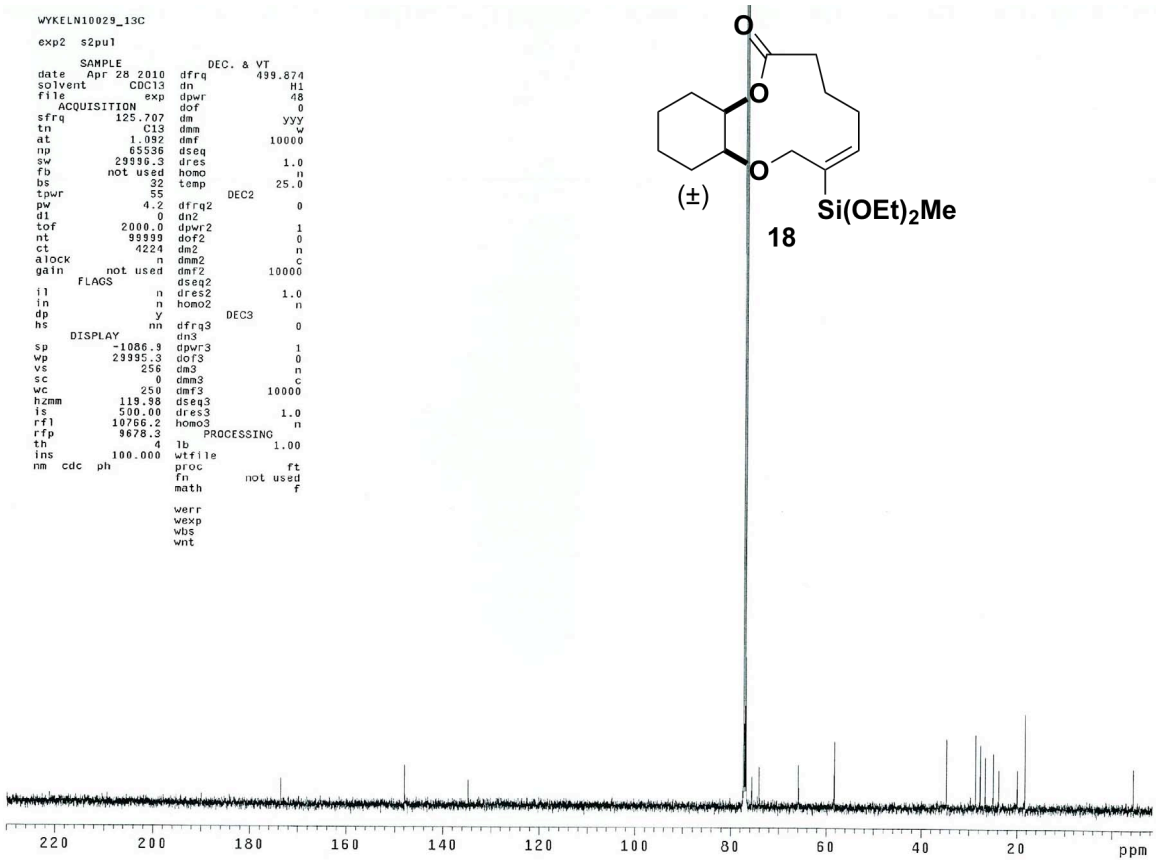

220
200
180
160
140
120
100
80
60
40
20
ppm

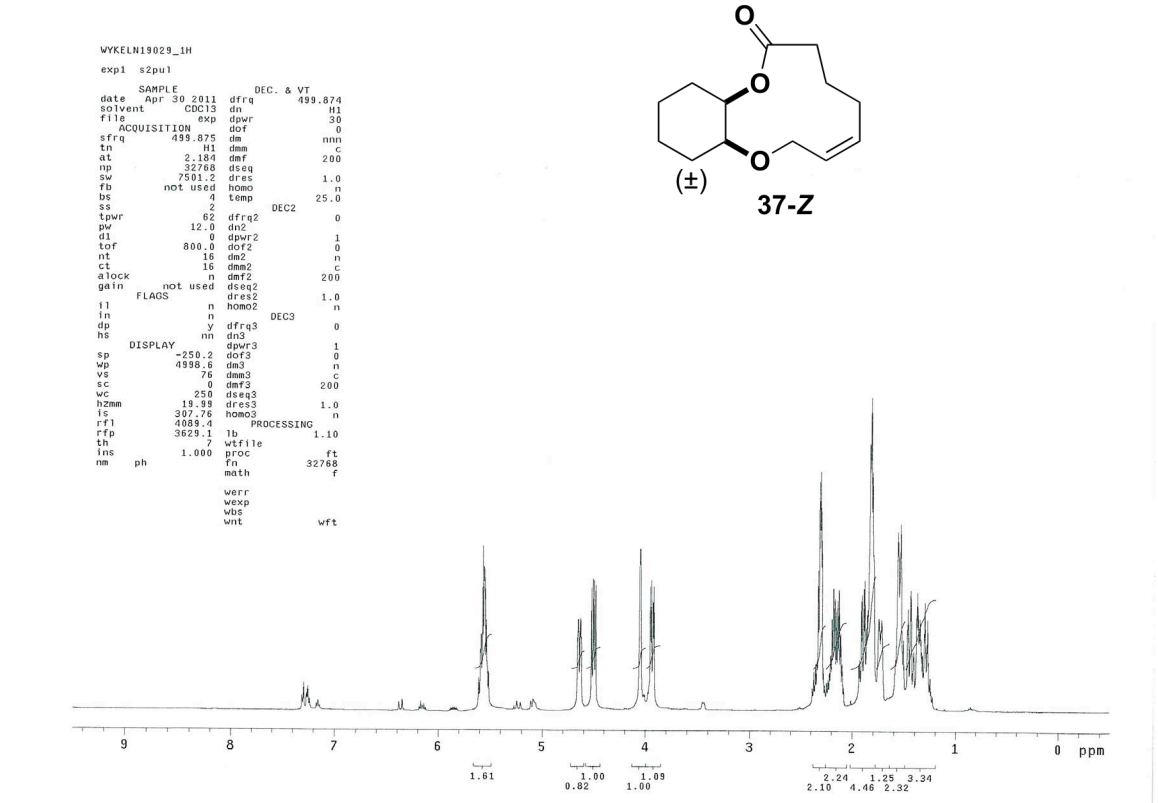

WYKELN8086_1H
exp1 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
O/Pub1/WYKELN8086_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 428.73
rfl 4090.3
rfp 3629.1
th 2
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
9
8
7
6
5
4
3
2
1
0
ppm
1.00 0.99
0.65
0.76
0.8163
2.00
1.00
3.04
1.89
1.81 1.13 3.39 4.50
1.14 2.95 2.23
2.37

O
O
O
(±)
Si(OEt)2Me

18'


WYKELN8086_13C
exp3 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 886
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 39
sc 0
wc 250
hzmm 119.88
is 500.00
rfl 1088.7
rfp 0
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
Si(OEt)2Me
18'
220
200
180
160
140
120
100
80
60
40
20
ppm
WYKELN10028_1H
exp1 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN10028~
_1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 109
sc 0
wc 250
hzmm 19.99
is 362.42
rfl 4090.3
rfp 3629.1
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
(±)
Si(OEt)2Me
18
9
8
7
6
5
4
3
2
1
0
ppm
0.84
0.90
0.99
3.12
2.06
1.00
3.08
2.09
3.58
8.17
2.11
1.15
2.32
2.38

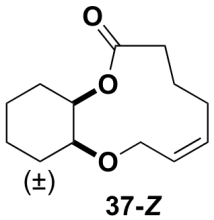

WYKELN10029_13C
exp2 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 4224
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1086.9
wp 29995.3
vs 256
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10766.2
rfp 9678.3
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
Si(OEt)2Me
18
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN19029_1H
exp1 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 76
sc 0
wc 250
hzmm 19.99
is 307.76
rfl 4089.4
rfp 3629.1
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
(±)
37-Z
9
8
7
6
5
4
3
2
1
0 ppm
1.61
1.00
0.82
1.09
1.00
2.24
2.10
1.25
4.46
3.34
2.32

WYKELN19029_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	8929
np	65536	dseq	
sw	29998.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.8	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	400	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1094.2	dpwr3	1
wp	29995.3	dof3	0
vs	30	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10773.5	homo3	n
rfp	9678.3	PROCESSING	
th	6	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



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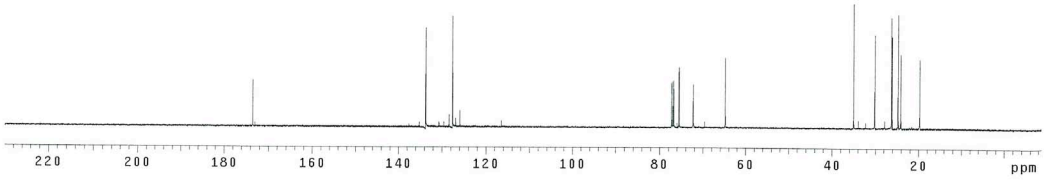
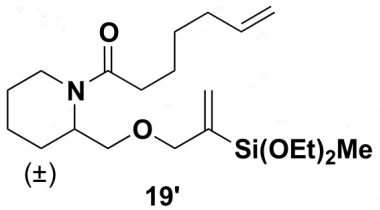
37-*Z*



WYKELN9044_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 21 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/i~	dof	0
	500c/schreiber/WAN~	dm	nnn
	G/Publ/WYKELN9044_~	dmm	c
	1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	24.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	32	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	154		
sc	0		
wc	250		
hzmm	19.99		
is	246.60		
rfl	4088.8		
rfp	3629.1		
th	7		
ins	2.000		
nm ph			



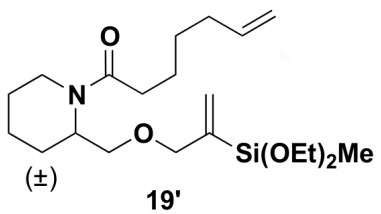
(±)

19'

WYKELN9044_13C_2

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 21 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	24.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1408	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1091.5	dpwr3	1
wp	29995.3	dof3	0
vs	72	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10770.7	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



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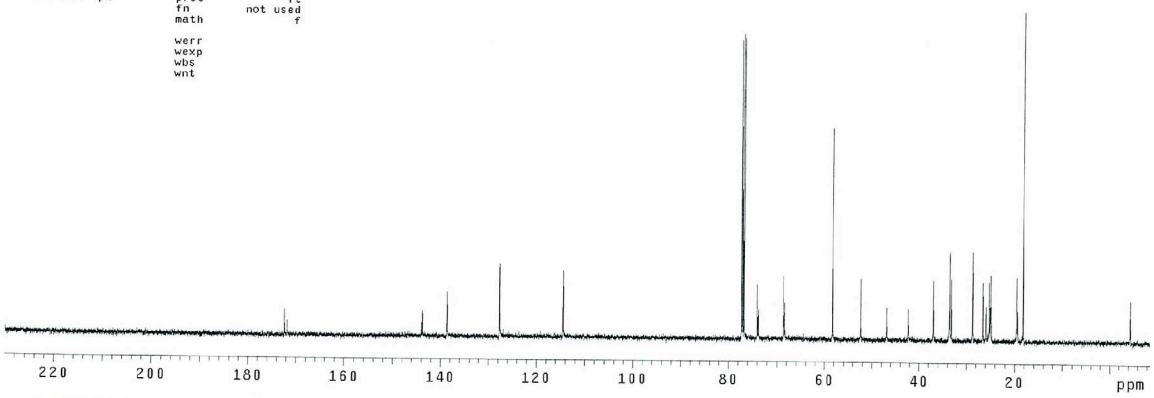
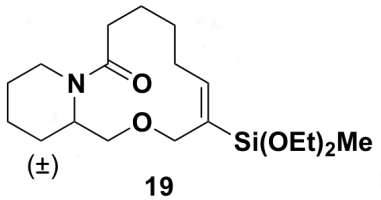
19'



WYKELN10035_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	May 22 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file /export/home/~		dpwr	30
ds2/vnmrsys/data/l~		dof	0
500c/schreiber/WAN~		dm	nnn
G/Publ/WYKELN10035~		dmm	c
1H.fid		dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	24.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0	werr	
d1	0	wexp	
tof	800.0	wbs	
nt	32	wnt	wft
ct	32		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	151		
sc	0		
wc	250		
hzmm	19.99		
is	258.16		
rfl	4089.8		
rfp	3629.1		
th	7		
ins	1.000		
nm ph			



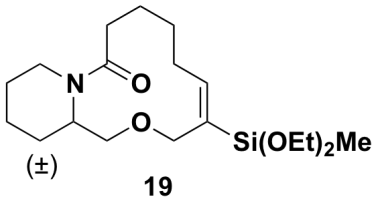
(±)

19

WYKELN10035_13C

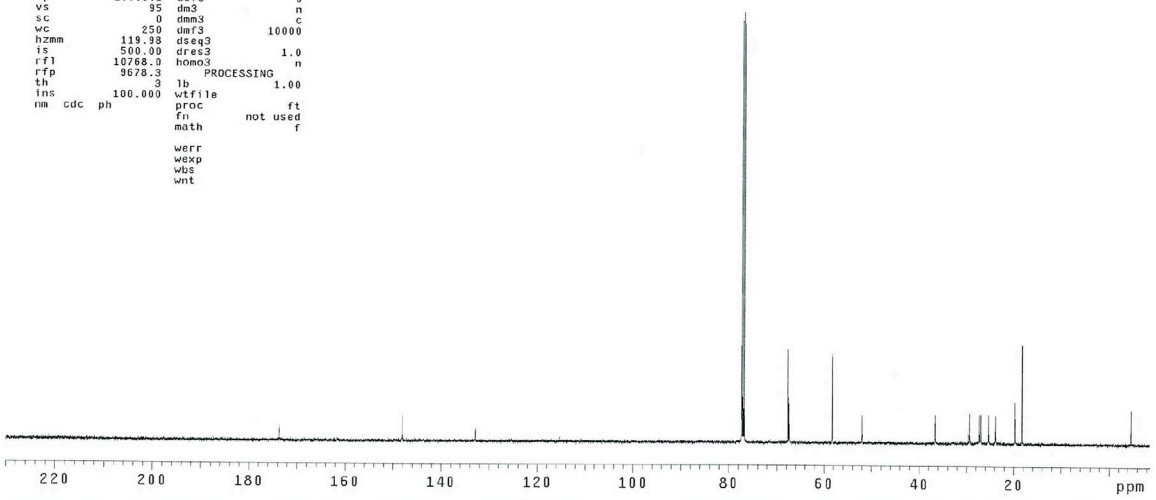
exp3 s2pul

SAMPLE		DEC. & VT	
date	May 22 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	24.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	3200	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1088.7	dpwr3	1
wp	29995.3	dof3	0
vs	95	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.0	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



(±)

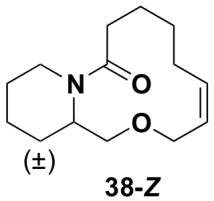
19



WYKELN19035_1H

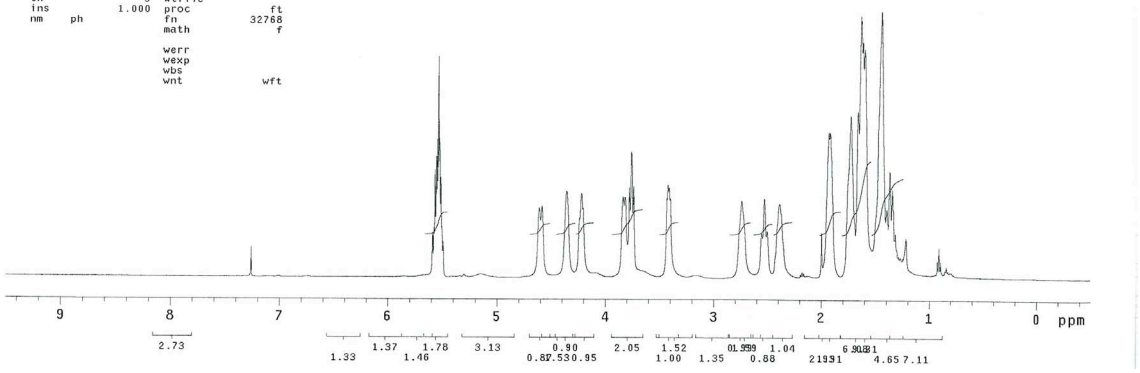
exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	16	dm2	n
ct	0	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	62	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	230.66	homo3	n
rfl	4089.4	PROCESSING	
rfp	3629.1	lb	1.10
th	5	wtfile	
ins	1.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft

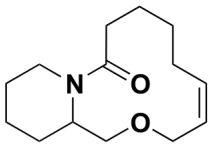


(±)

38-*Z*

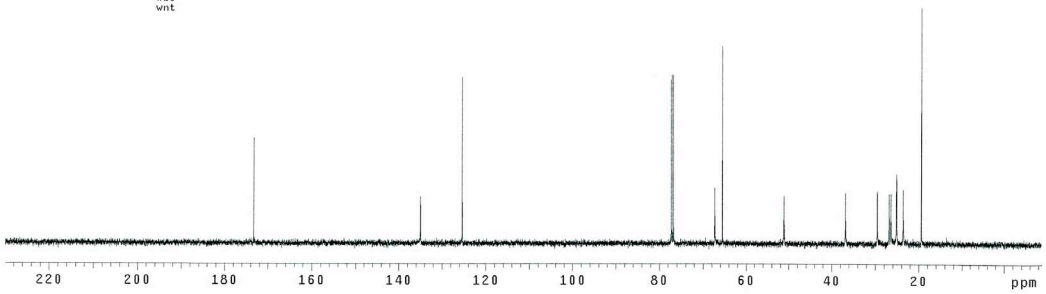


```
WYKELN19035_13C

exp2  s2pul

      SAMPLE
date   Apr 30 2011
solvent      CDCl3
file            exp
    ACQUISITION
sfrq        125.707
tn              C13
at              1.092
np             65536
sw           29996.3
fb          not used
bs                16
tpwr              55
pw               4.8
d1                 0
tof           2000.0
nt              9999
ct                 0
alock              n
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp            -1097.0
wp           29995.3
vs                57
sc                 0
wc               250
hzmm          119.98
is            500.00
rfl          10776.2
rfp           9678.3
th                 5
ins           100.000
nm  cdc  ph

          DEC. & VT
dfrq         499.874
dn                H1
dpwr              48
dof                0
dm               yyy
dmm                w
dmf             8929
dseq
dres              1.0
homo                n
temp             25.0
          DEC2
dfrq2              0
dn2
dpwr2              1
dof2               0
dm2                n
dmm2               c
dmf2           10000
dseq2
dres2             1.0
homo2               n
          DEC3
dfrq3              0
dn3
dpwr3              1
dof3               0
dm3                n
dmm3               c
dmf3           10000
dseq3
dres3             1.0
homo3               n
     PROCESSING
lb                1.00
wtfile
proc                ft
fn          not used
math                f

werr
wexp
wbs
wnt
```

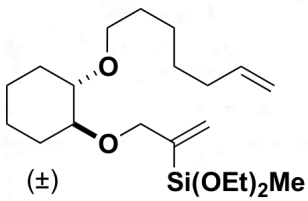


(±)

38-*Z*

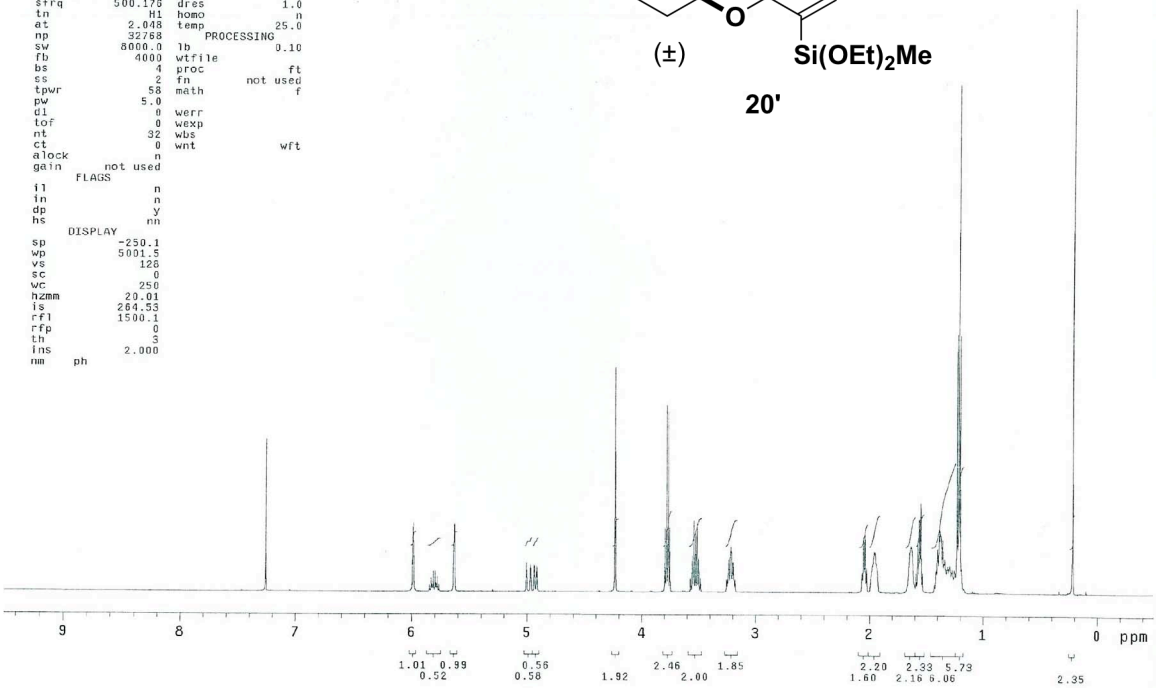



```
WYKELN8082_1H

exp1  s2pul

      SAMPLE
date   Apr 24 2010
solvent      CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500b/schreiber/WAN~
G/Pub1/WYKELN8082_~
          1H.fid
    ACQUISITION
sfrq        500.176
tn               H1
at             2.048
np             32768
sw            8000.0
fb              4000
bs                 4
ss                 2
tpwr              58
pw               5.0
d1                 0
tof                0
nt                32
ct                 0
alock              n
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp            -250.1
wp           5001.5
vs                128
sc                 0
wc               250
hzmm           20.01
is            264.53
rfl           1500.1
rfp                0
th                 3
ins            2.000
nm    ph

          DEC. & VT
dfrq         500.176
dn                H1
dpwr              32
dof                0
dm               nnn
dmm                c
dmf             8770
dseq
dres              1.0
homo                n
temp             25.0
     PROCESSING
lb                0.10
wtfile
proc                ft
fn          not used
math                f

werr
wexp
wbs
wnt             wft
```



(±) $Si(OEt)_2Me$

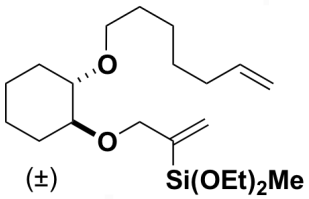
20'



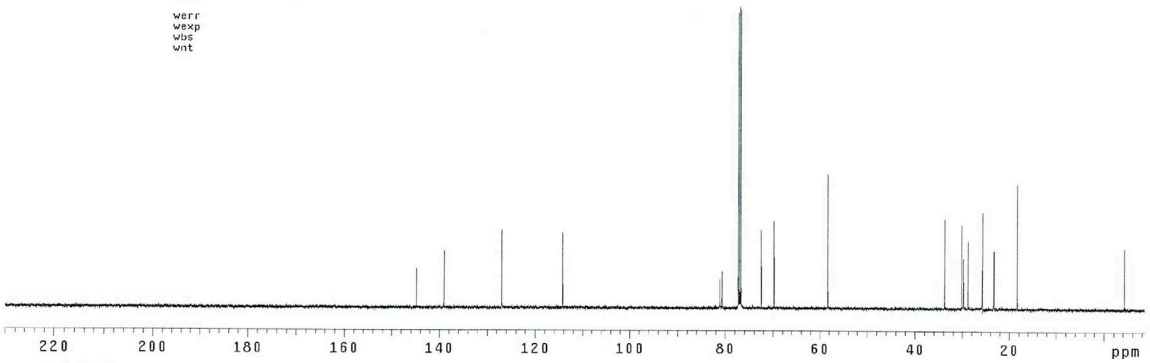
WYKELN8082_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 25 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	2.0	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	1656	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1087.8	dpwr3	1
wp	29995.3	dof3	0
vs	67	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	1088.7	homo3	n
rfp	0	PROCESSING	
th	4	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



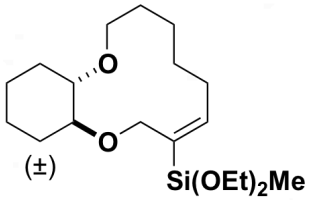
20'



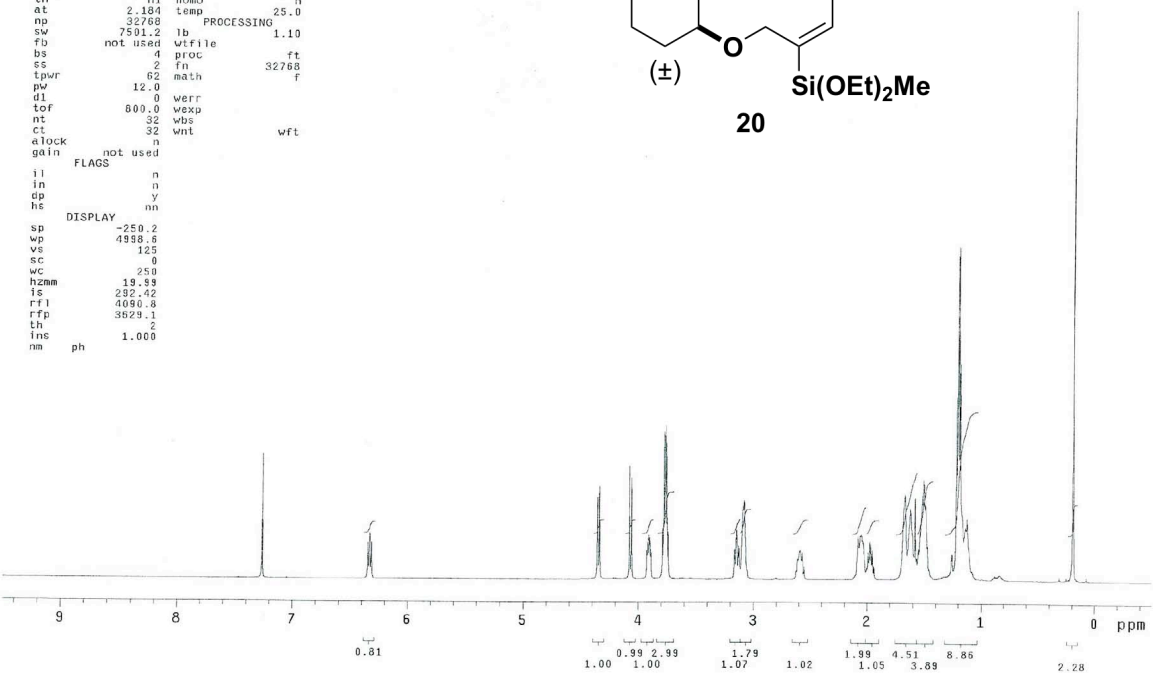
WYKELN10025_1H

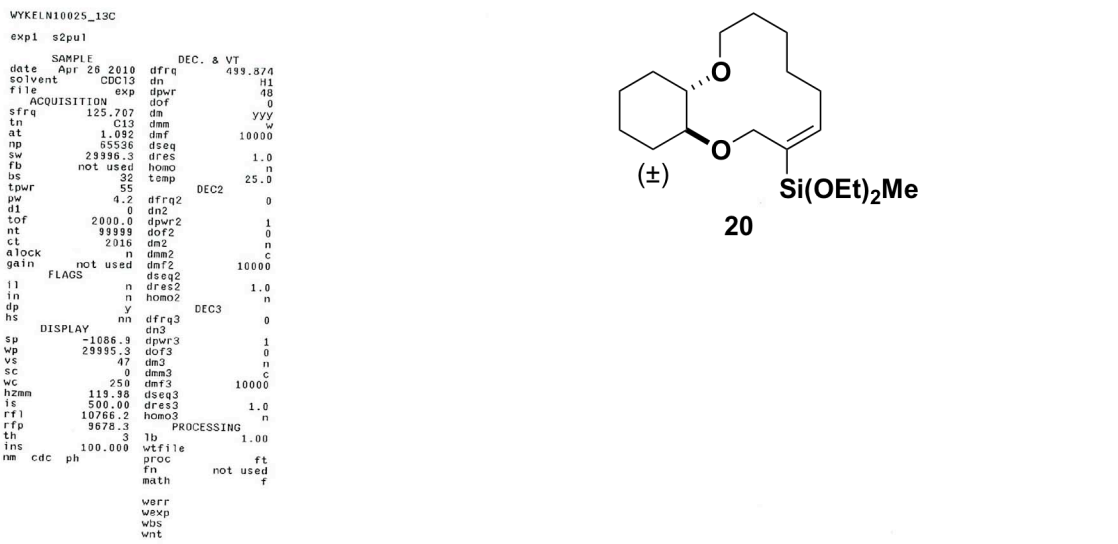
exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 26 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/i~	dof	0
	500c/schreiber/WAN~	dm	nnn
	G/Pub1/WYKELN10025~	dmm	c
	1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0	werr	
d1	0	wexp	
tof	800.0	wbs	
nt	32	wnt	wft
ct	32		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	125		
sc	0		
wc	250		
hzmm	19.99		
is	292.42		
rfl	4090.8		
rfp	3829.1		
th	2		
ins	1.000		
nm ph			

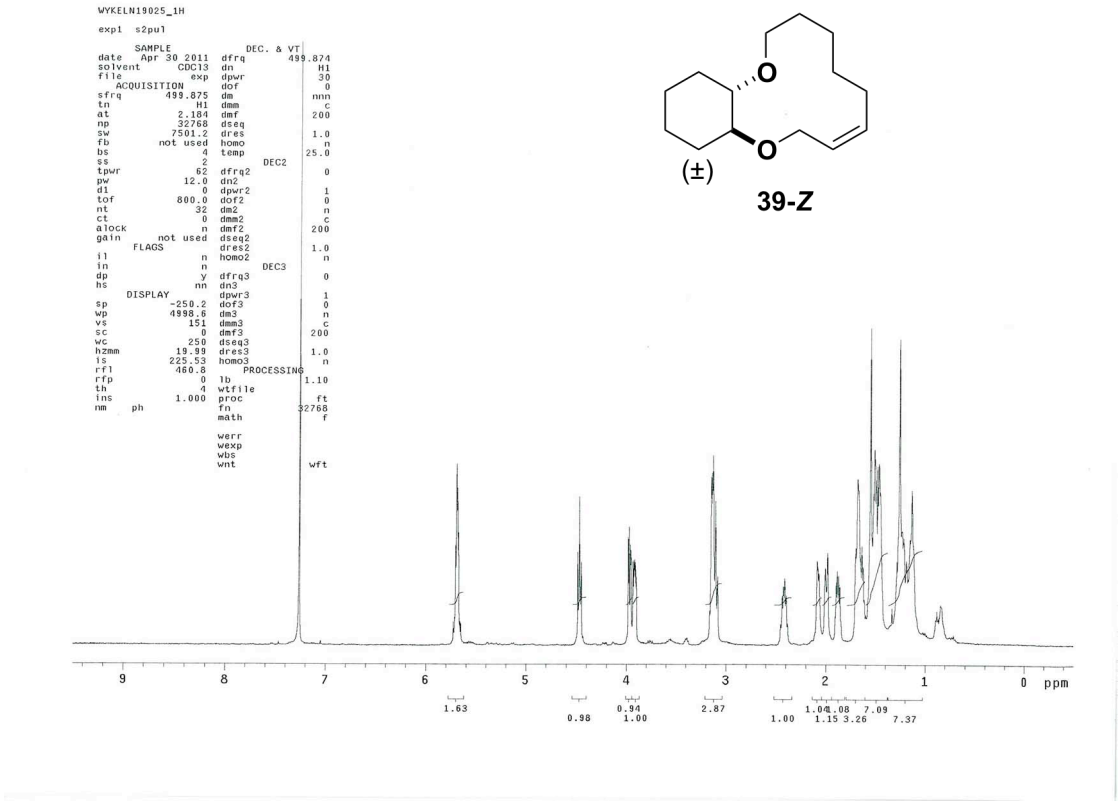


20




WYKELN10025_13C
exp1 s2pul
SAMPLE
date Apr 26 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 2016
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1086.9
wp 29995.3
vs 47
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10766.2
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
(±)
Si(OEt)2Me
220
200
180
160
140
120
100
80
60
40
20
ppm

20

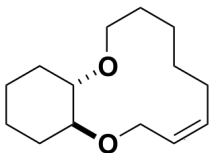

WYKELN19025_1H
exp1 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 225.53
rfl 460.8
rfp 0
th 4
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
(±)
9
8
7
6
5
4
3
2
1
0 ppm
1.63
0.98
0.94
1.00
2.87
1.00
1.04
1.15
1.08
3.26
7.09
7.37

39-*Z*

WYKELN19025_13C

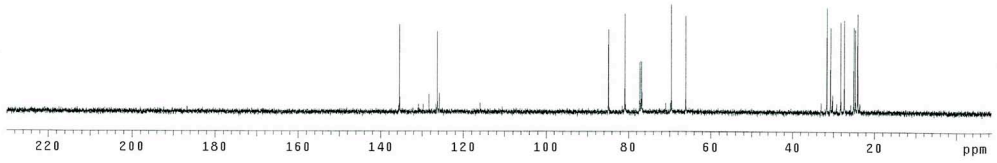
exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	8929
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.8	dfrq2	0
dl	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	0	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1095.1	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10774.4	homo3	n
rfp	9678.3	PROCESSING	
th	10	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



(±)

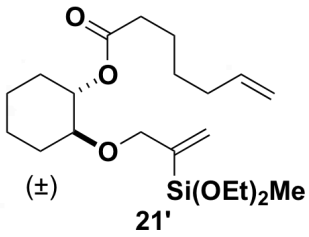
39-*Z*



WYKELN8090_1H

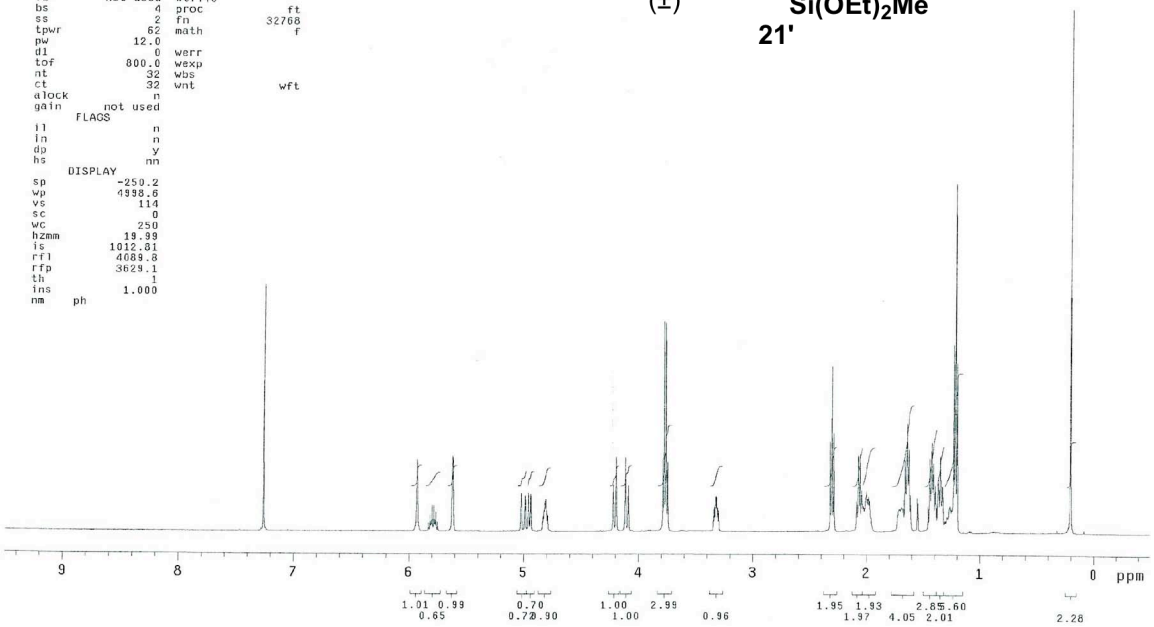
exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 29 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
ds2/vnmrsys/data/i~		dof	0
500C/schreiber/WAN~		dm	nnn
G/Pub1/WYKELN8090_~		dmm	c
1H.fid		dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
dl	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	32	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	114		
sc	0		
wc	250		
hzmm	19.99		
is	1012.81		
rfl	4089.8		
rfp	3629.1		
th	1		
ins	1.000		
nm ph			



(±) $Si(OEt)_2Me$

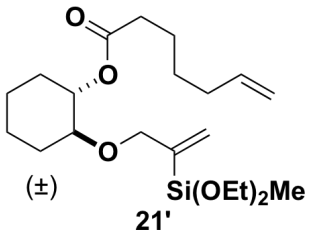
21'



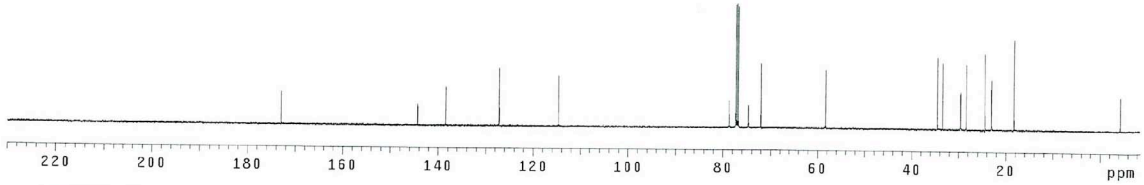
WYKELN8090_13C

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 29 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1280	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1087.8	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10767.1	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



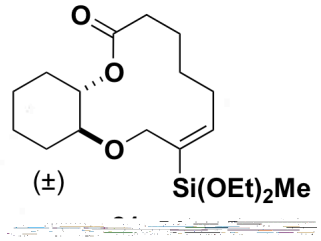
21'



WYKELN10033_1H

exp1 s2pul

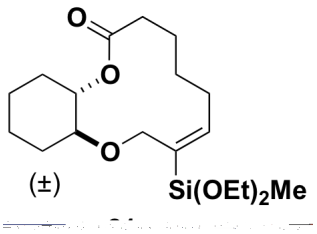
SAMPLE		DEC. & VT	
date	Apr 30 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/i~	dof	0
	500c/schraiber/WAN~	dm	nnn
	G/Pub1/WYKELN10033~	dmm	c
	1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	32	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	151		
sc	0		
wc	250		
hzmm	19.99		
is	299.18		
rfl	4083.8		
rfp	3629.1		
th	3		
ins	1.000		
nm ph			

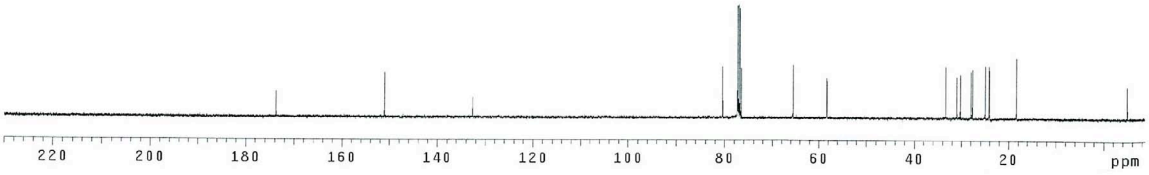


WYKELN10033_13C

exp3 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	800	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1087.8	dpwr3	1
wp	29995.3	dof3	0
vs	25	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10767.1	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	

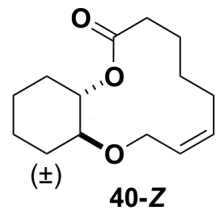




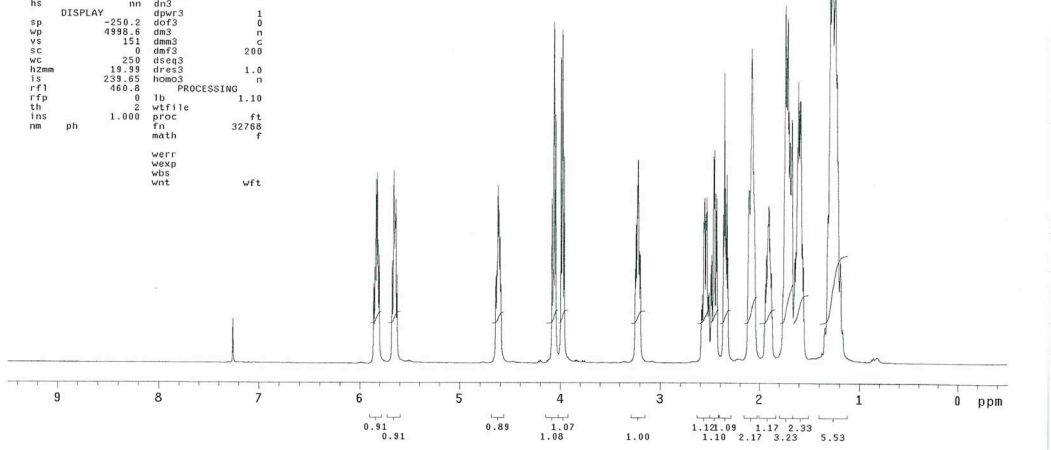
WYKELN19033_1H

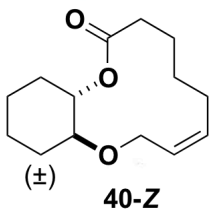
exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	16	dm2	n
ct	0	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	151	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	239.65	homo3	n
rfl	460.8	PROCESSING	
rfp	0	lb	1.10
th	2	wtfile	
ins	1.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft



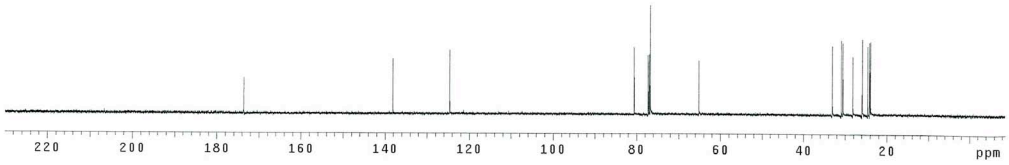
40-*Z*



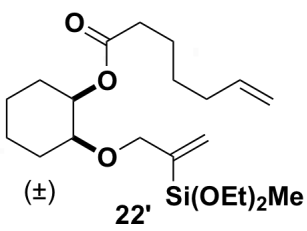


40-*Z*

```
WYKELN19033_13C

exp2  s2pul

        SAMPLE
date    Apr 30 2011
solvent       CDCl3
file             exp
     ACQUISITION
sfrq         125.707
tn               C13
at             1.092
np             65536
sw           29996.3
fb           not used
bs                16
tpwr              55
pw               4.8
d1                 0
tof           2000.0
nt              9999
ct                 0
alock              n
gain         not used
       FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -1092.4
wp           29995.3
vs                27
sc                 0
wc               250
hzmm          119.98
is            500.00
rfl          10771.7
rfp           9678.3
th                 4
ins           100.000
nm  cdc  ph

          DEC. & VT
dfrq         499.874
dn                H1
dpwr              48
dof                0
dm               yyy
dmm                w
dmf             8929
dseq
dres             1.0
homo               n
temp            25.0
          DEC2
dfrq2              0
dn2
dpwr2              1
dof2               0
dm2                n
dmm2               c
dmf2           10000
dseq2
dres2            1.0
homo2              n
          DEC3
dfrq3              0
dn3
dpwr3              1
dof3               0
dm3                n
dmm3               c
dmf3           10000
dseq3
dres3            1.0
homo3              n
     PROCESSING
lb                1.00
wtfile
proc              ft
fn          not used
math               f

werr
wexp
wbs
wnt
```




```
WYKELN8088_1H

exp1  s2pul

        SAMPLE
date    Apr 28 2010
solvent       CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500c/schreiber/WAN~
G/Publ/WYKELN8088_~
              1H.fid
     ACQUISITION
sfrq         499.875
tn                H1
at            2.184
np            32768
sw           7501.2
fb         not used
bs                 4
ss                 2
tpwr              62
pw              12.0
d1                 0
tof            800.0
nt                32
ct                32
alock              n
gain         not used
       FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -250.2
wp           4998.6
vs              151
sc                 0
wc               250
hzmm           19.99
is            368.14
rfl           4080.8
rfp           3629.1
th                 3
ins           2.000
nm     ph

          DEC. & VT
dfrq         499.874
dn                H1
dpwr              30
dof                0
dm               nnn
dmm                c
dmf              200
dseq
dres             1.0
homo               n
temp            25.0
     PROCESSING
lb                1.10
wtfile
proc              ft
fn             32768
math               f
werr
wexp
wbs
wnt              wft
```

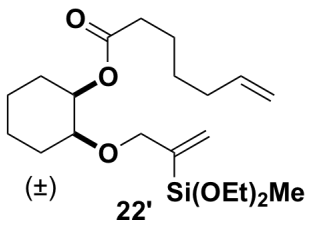


22' **Si(OEt)$_2$Me**

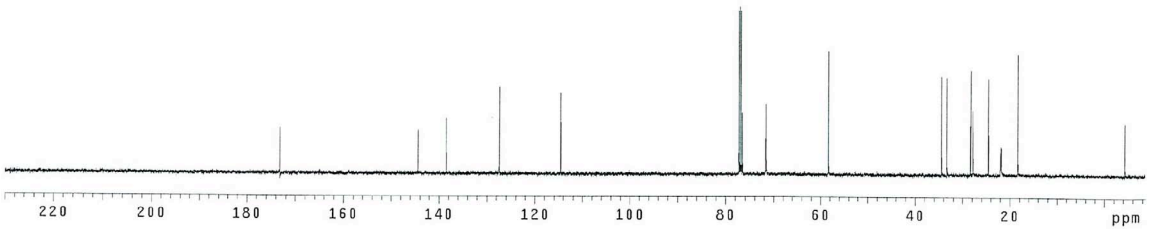
WYKELN8088_13C

exp3 s2pul

SAMPLE		DEC. & VT	
date	Apr 28 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	736	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1087.8	dpwr3	1
wp	29995.3	dof3	0
vs	37	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.88	dseq3	
is	500.00	dres3	1.0
rfl	1088.7	homo3	n
rfp	0	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



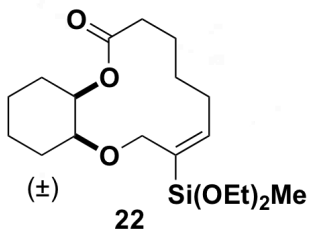
22'



WYKELN10031_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	30
	ds2/vnmrsys/data/i~	dof	0
	500c/schreiber/WAN~	dm	nnn
	G/Pub1/WYKELN10031~	dmm	c
	1H.fid	dmf	200
ACQUISITION		dseq	
sfrq	499.875	dres	1.0
tn	H1	homo	n
at	2.184	temp	25.0
np	32768	PROCESSING	
sw	7501.2	lb	1.10
fb	not used	wtfile	
bs	4	proc	ft
ss	2	fn	32768
tpwr	62	math	f
pw	12.0		
d1	0	werr	
tof	800.0	wexp	
nt	32	wbs	
ct	32	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	4998.6		
vs	130		
sc	0		
wc	250		
hzmm	19.99		
is	434.36		
rfl	4089.8		
rfp	3629.1		
th	7		
ins	100.000		
nm ph			

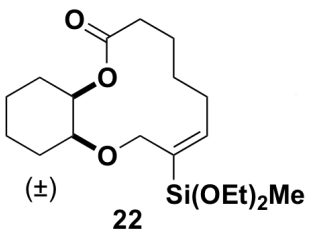


22

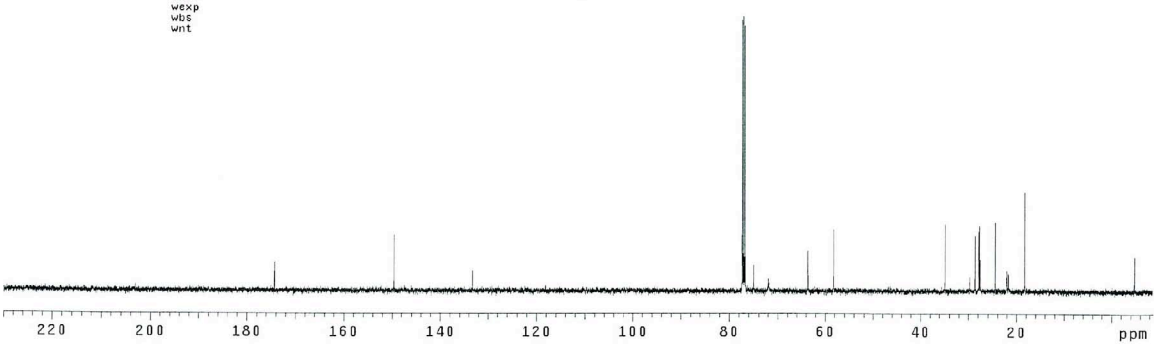
WYKELN10031_13C

exp3 s2pul

SAMPLE		DEC. & VT	
date	Apr 30 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	10000
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	32	temp	25.0
tpwr	55	DEC2	
pw	4.2	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1856	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1086.9	dpwr3	1
wp	29995.3	dof3	0
vs	60	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	1087.8	homo3	n
rfp	0	PROCESSING	
th	2	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



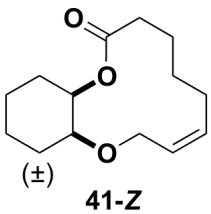
22



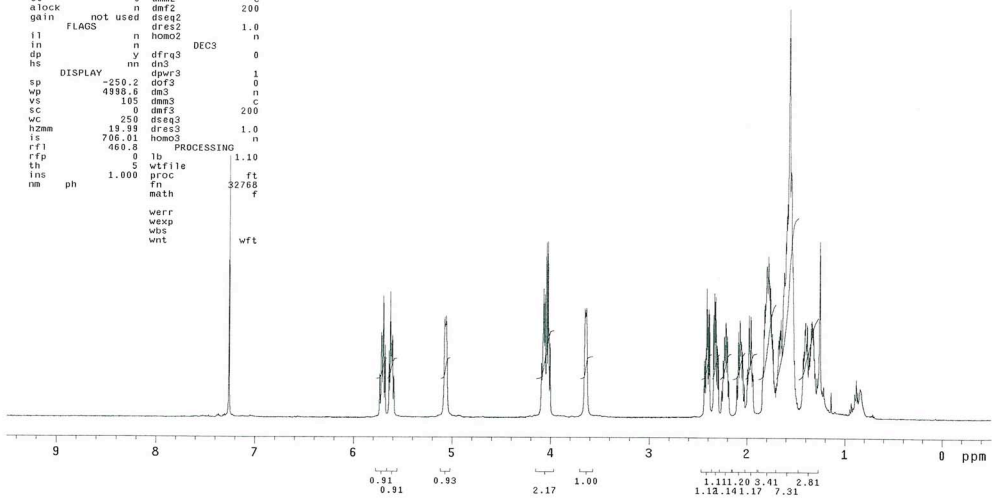
WYKELN19030_1H

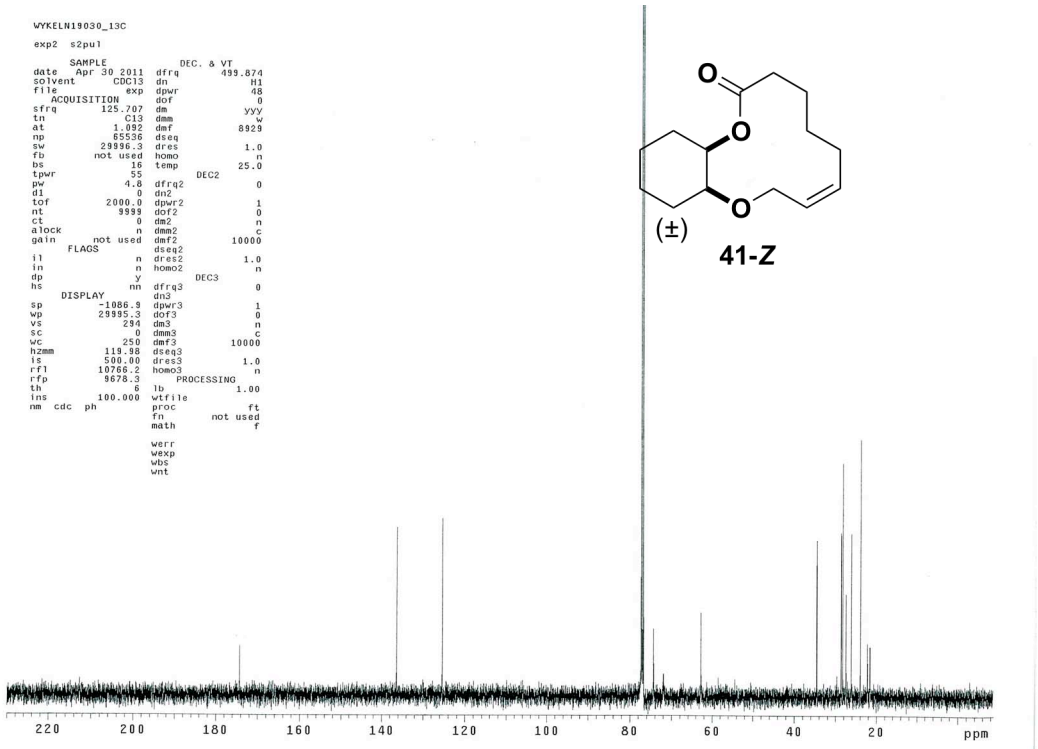
exp1 s2pul

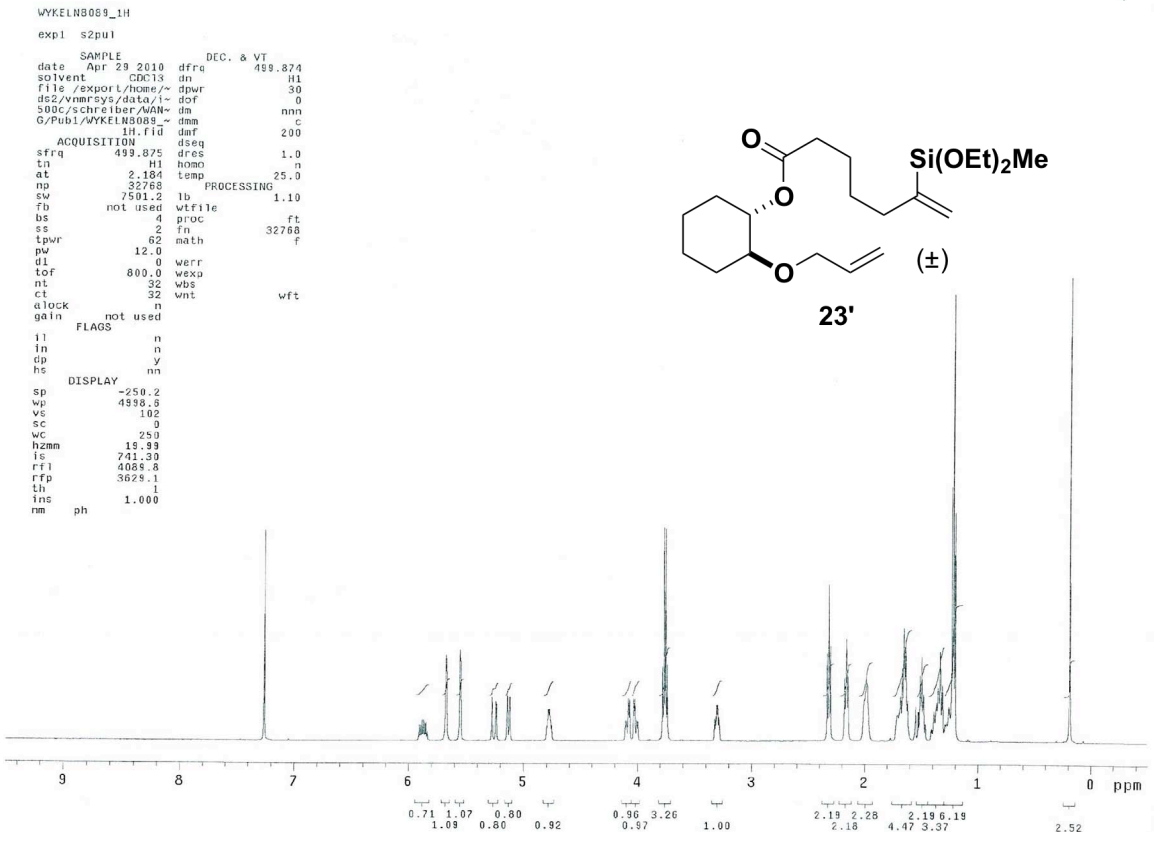
SAMPLE		DEC. & VT	
date	Apr 30 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	16	dm2	n
ct	0	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	105	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	706.01	homo3	n
rfl	460.8	PROCESSING	
rfp	0	lb	1.10
th	5	wtfile	
ins	1.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft

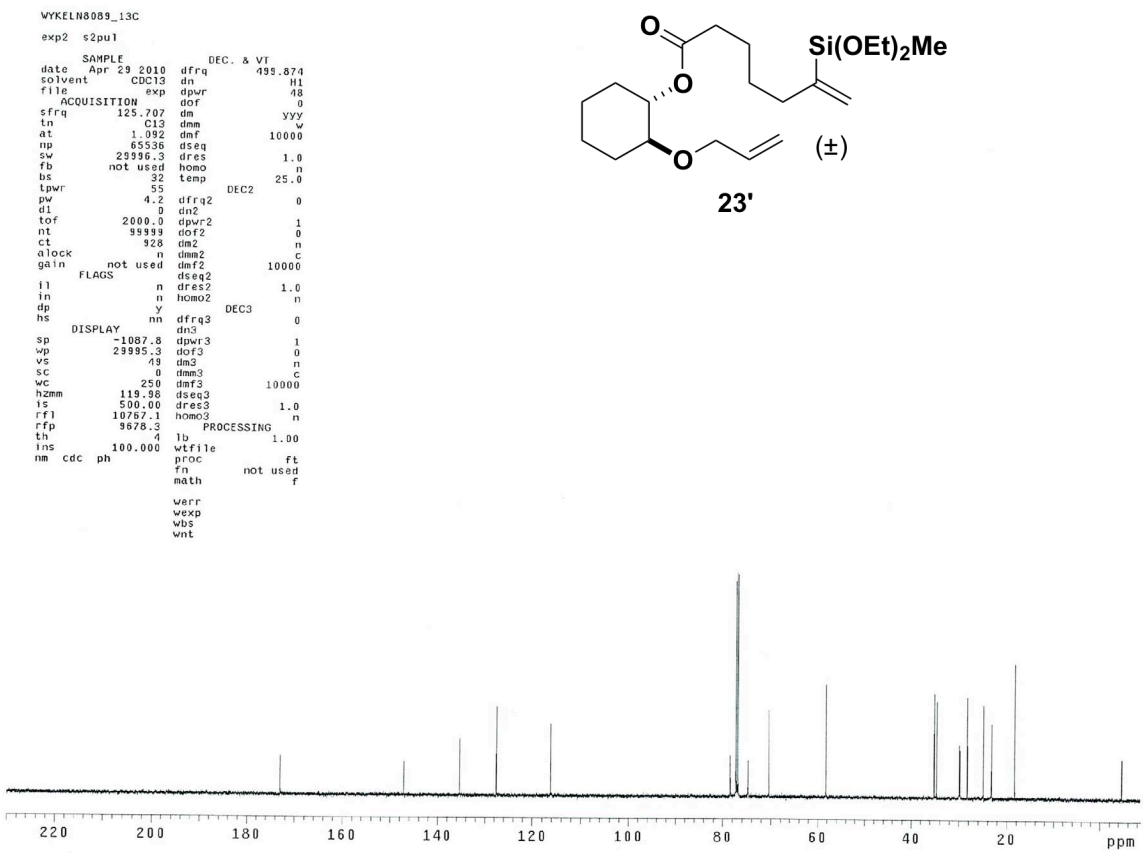


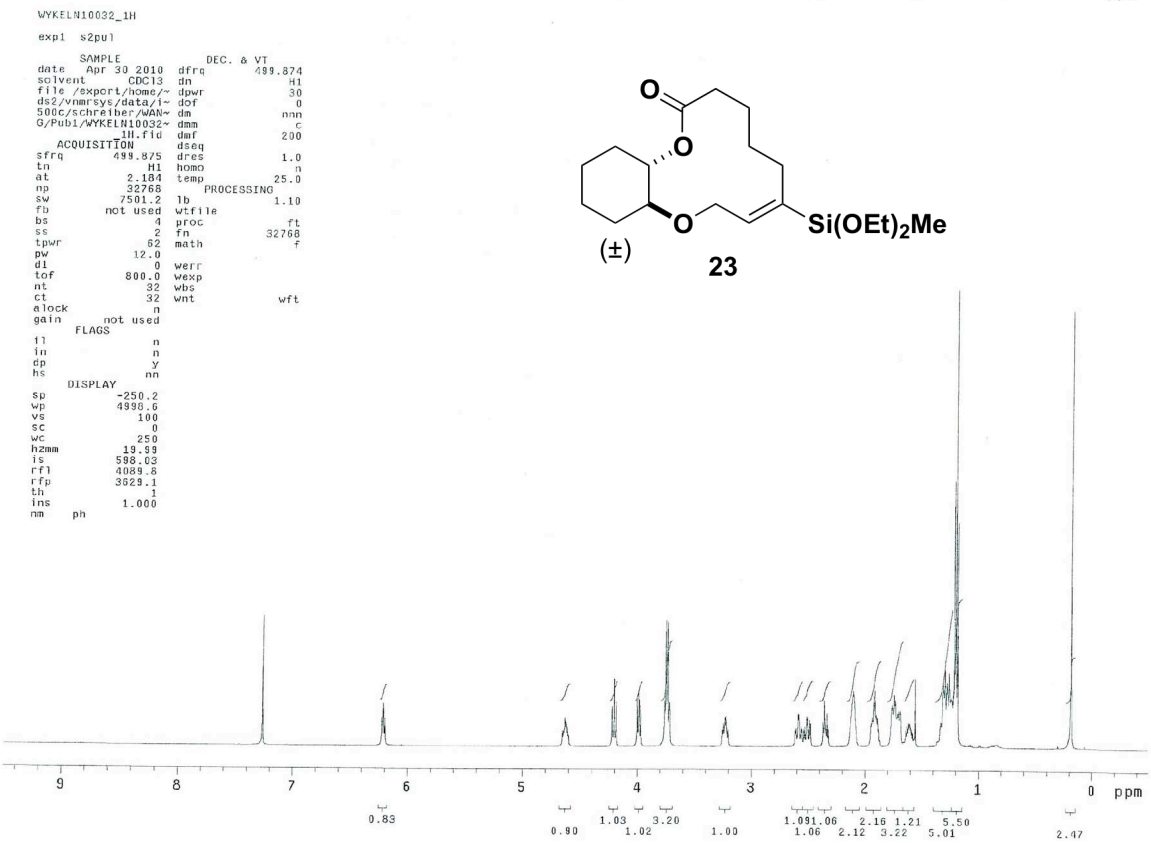
41-*Z*



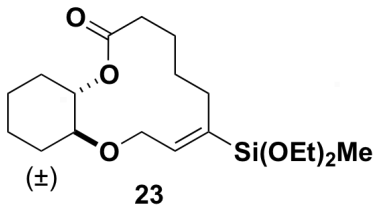

WYKELN19030_13C
exp2 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1086.9
wp 29995.3
vs 294
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10766.2
rfp 9678.3
th 6
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
41-Z
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN8089_1H
exp1 s2pul
SAMPLE
date Apr 29 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN8089_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.5
vs 102
sc 0
wc 250
hzmm 19.99
is 741.30
rfl 4088.8
rfp 3629.1
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
(±)
23'
9
8
7
6
5
4
3
2
1
0 ppm
0.71 1.07 0.80
1.09 0.80 0.92
0.96 3.26
0.97 1.00
2.19 2.28 2.19 6.19
2.18 4.47 3.37
2.52

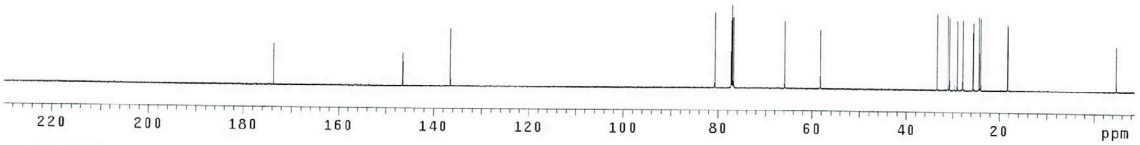

WYKELN8089_13C
exp2 s2pul
SAMPLE
date Apr 29 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 928
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 49
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)2Me
(±)
23'
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN10032_1H
exp1 s2pul
SAMPLE
date Apr 30 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Publ/WYKELN10032~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 52
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 100
sc 0
wc 250
hzmm 19.99
is 598.03
rfl 4089.8
rfp 3629.1
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
(±)
23
9
8
7
6
5
4
3
2
1
0
ppm
0.83
0.90
1.03
1.02
3.20
1.00
1.09
1.06
1.06
2.12
2.16
3.22
1.21
5.01
5.50
2.47

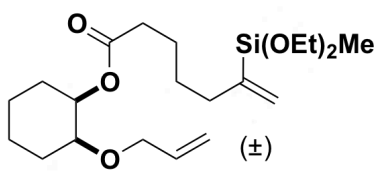
```
WYKELN10032_13C

exp3  s2pul

      SAMPLE
date   Apr 30 2010
solvent       CDCl3
file             exp
   ACQUISITION
sfrq        125.707
tn              C13
at              1.092
np              65536
sw            29996.3
fb          not used
bs                32
tpwr              55
pw               4.2
d1                 0
tof           2000.0
nt             99999
ct              1216
alock              n
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp            -1090.6
wp            29995.3
vs                 18
sc                  0
wc                250
hzmm           119.98
is             500.00
rfl           10769.8
rfp            9678.3
th                 4
ins            100.000
nm  cdc  ph

      DEC. & VT
dfrq          499.874
dn                H1
dpwr              48
dof                0
dm               yyy
dmm                w
dmf            10000
dseq
dres             1.0
homo               n
temp            25.0
      DEC2
dfrq2              0
dn2
dpwr2              1
dof2               0
dm2                n
dmm2               c
dmf2           10000
dseq2
dres2            1.0
homo2              n
      DEC3
dfrq3              0
dn3
dpwr3              1
dof3               0
dm3                n
dmm3               c
dmf3           10000
dseq3
dres3            1.0
homo3              n
     PROCESSING
lb               1.00
wtfile
proc             ft
fn           not used
math              f

werr
wexp
wbs
wnt
```



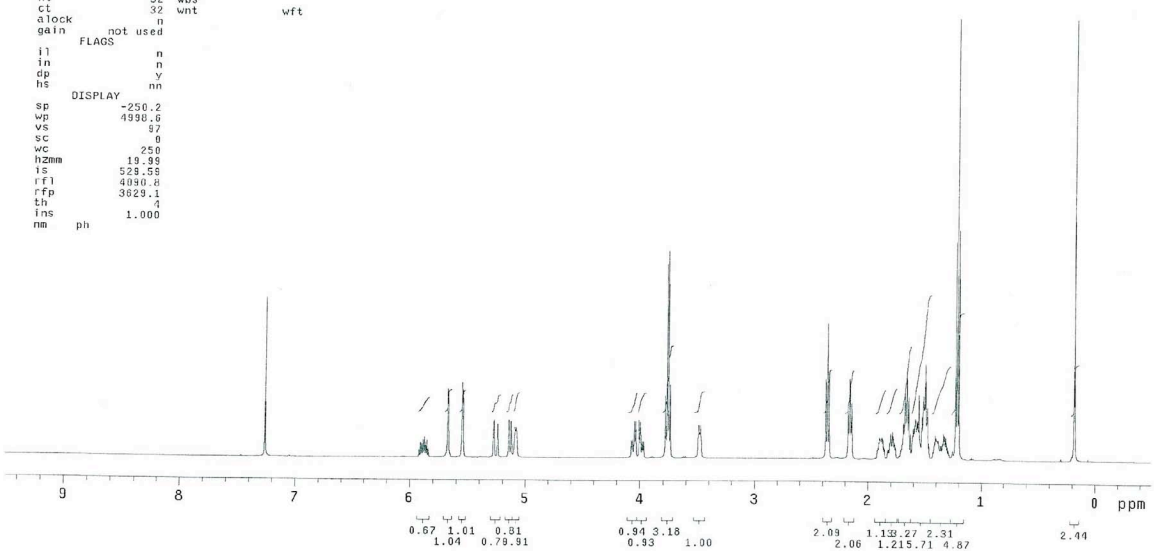
23

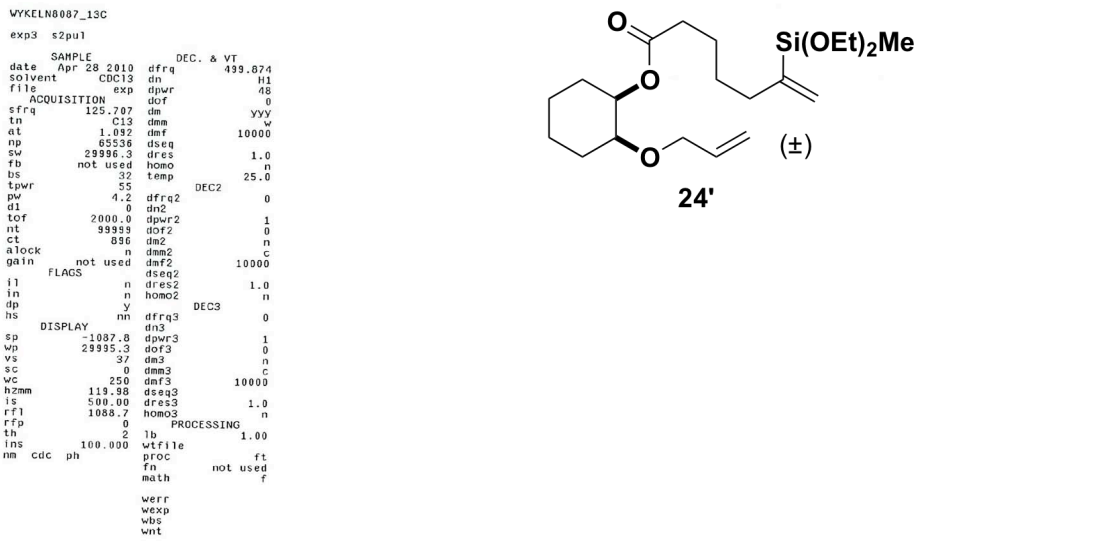


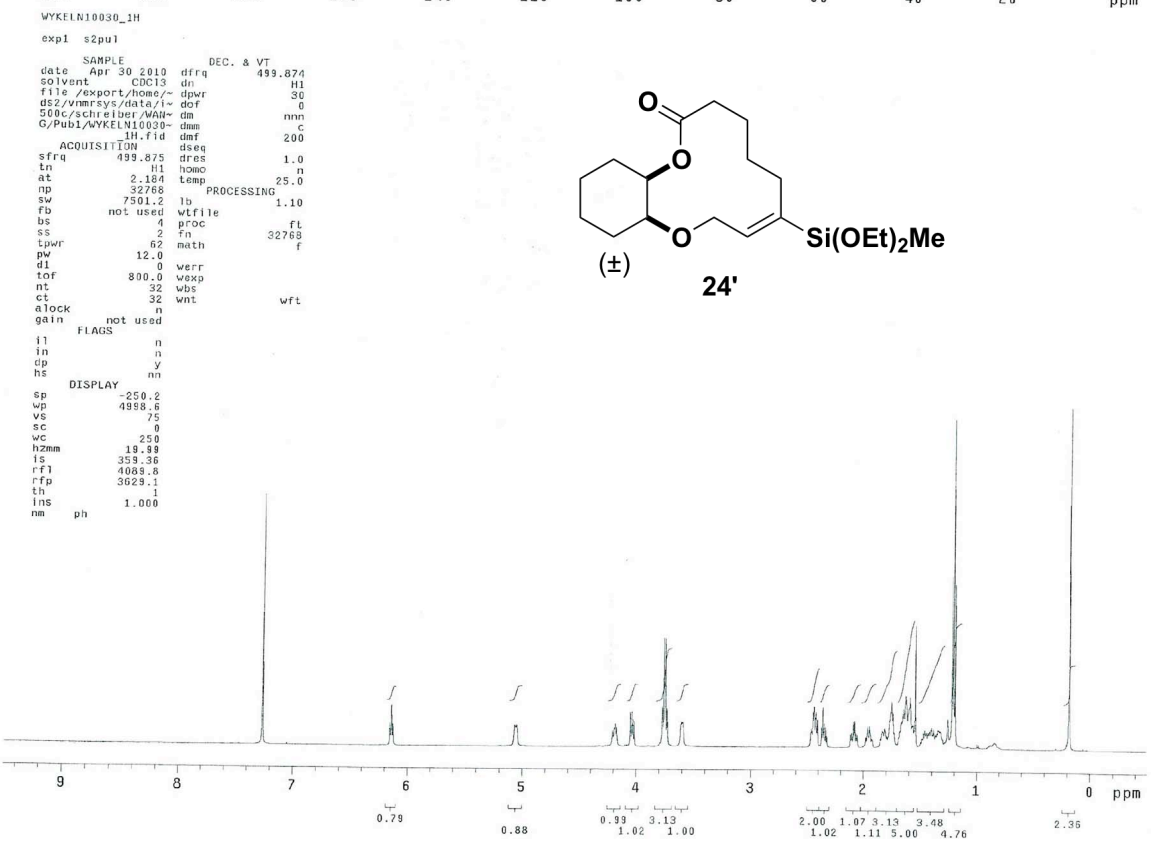

```
WYKELN8087_1H

exp1  s2pul

      SAMPLE
date   Apr 28 2010
solvent       CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500c/schreiber/WAN~
G/Publ/WYKELN8087_~
            1H.fid
   ACQUISITION
sfrq          499.875
tn                H1
at             2.184
np             32768
sw            7501.2
fb          not used
bs                 4
ss                 2
tpwr              52
pw              12.0
d1                 0
tof            800.0
nt                32
ct                32
alock              n
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp             -250.2
wp            4998.6
vs                 97
sc                  0
wc                250
hzmm           19.99
is             528.58
rfl           4090.8
rfp           3029.1
th                 4
ins            1.000
nm    ph

      DEC. & VT
dfrq          499.874
dn                H1
dpwr              30
dof                0
dm              nnn
dmm                c
dmf              200
dseq
dres             1.0
homo               n
temp            25.0
     PROCESSING
lb               1.10
wtfile
proc             ft
fn           32768
math              f

werr
wexp
wbs
wnt              wft
```

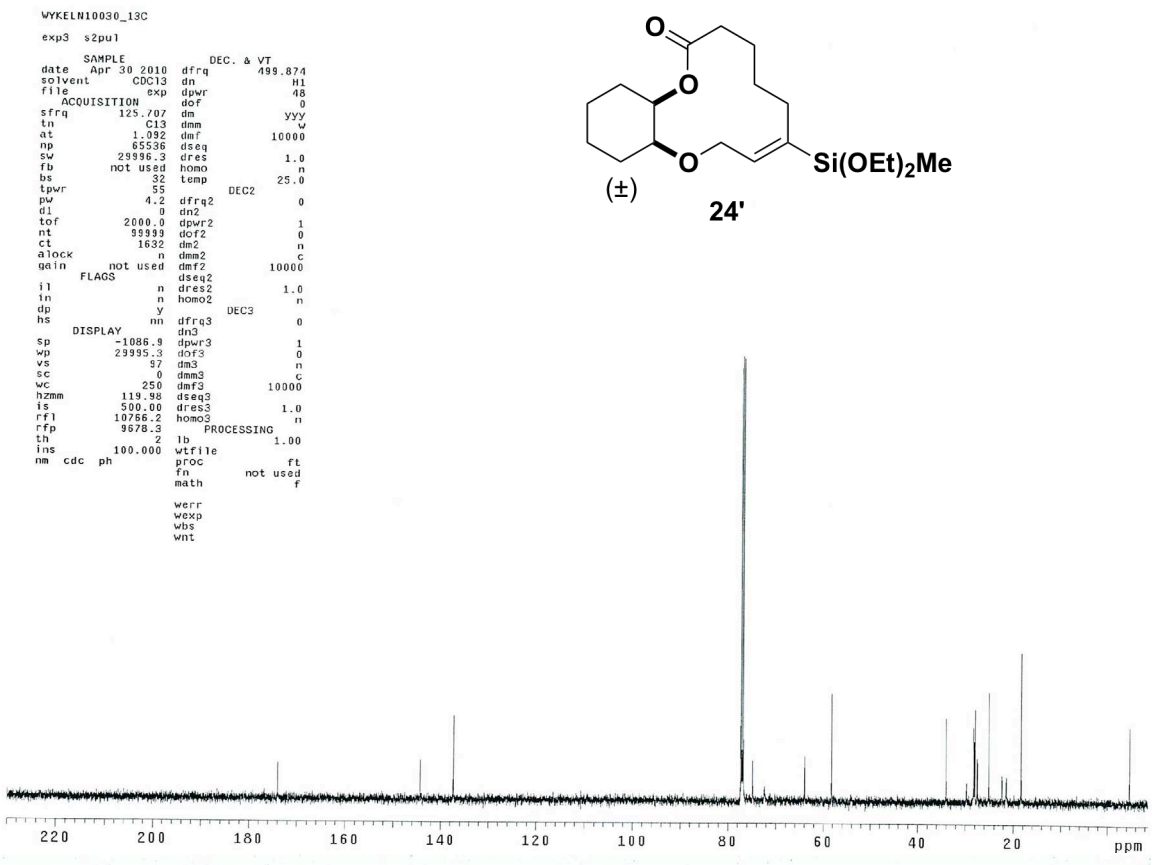


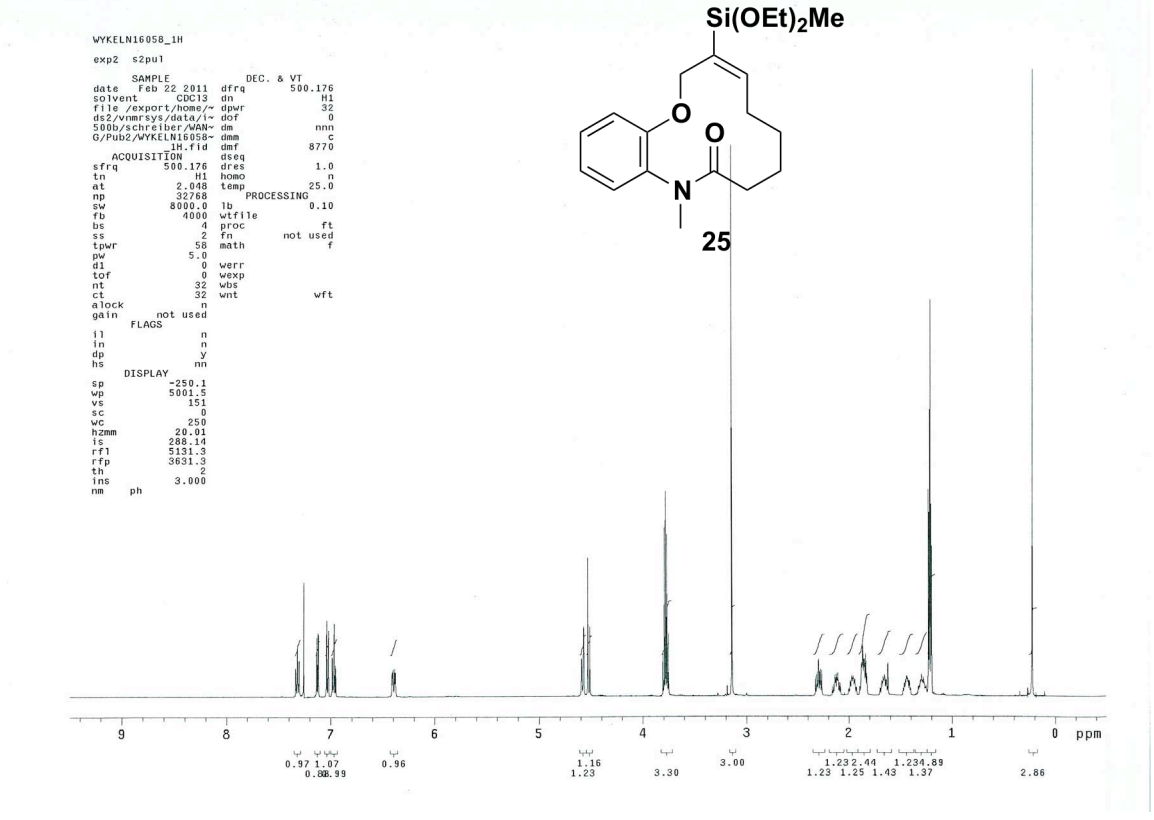
24'

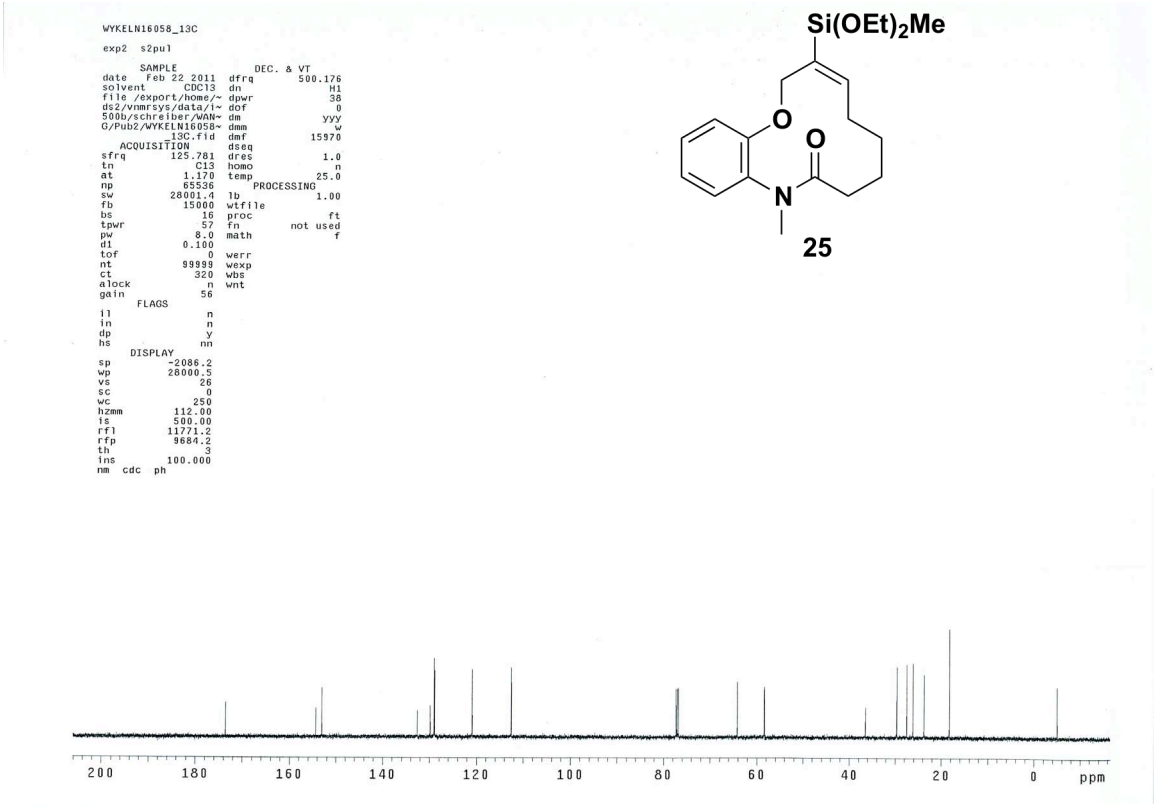


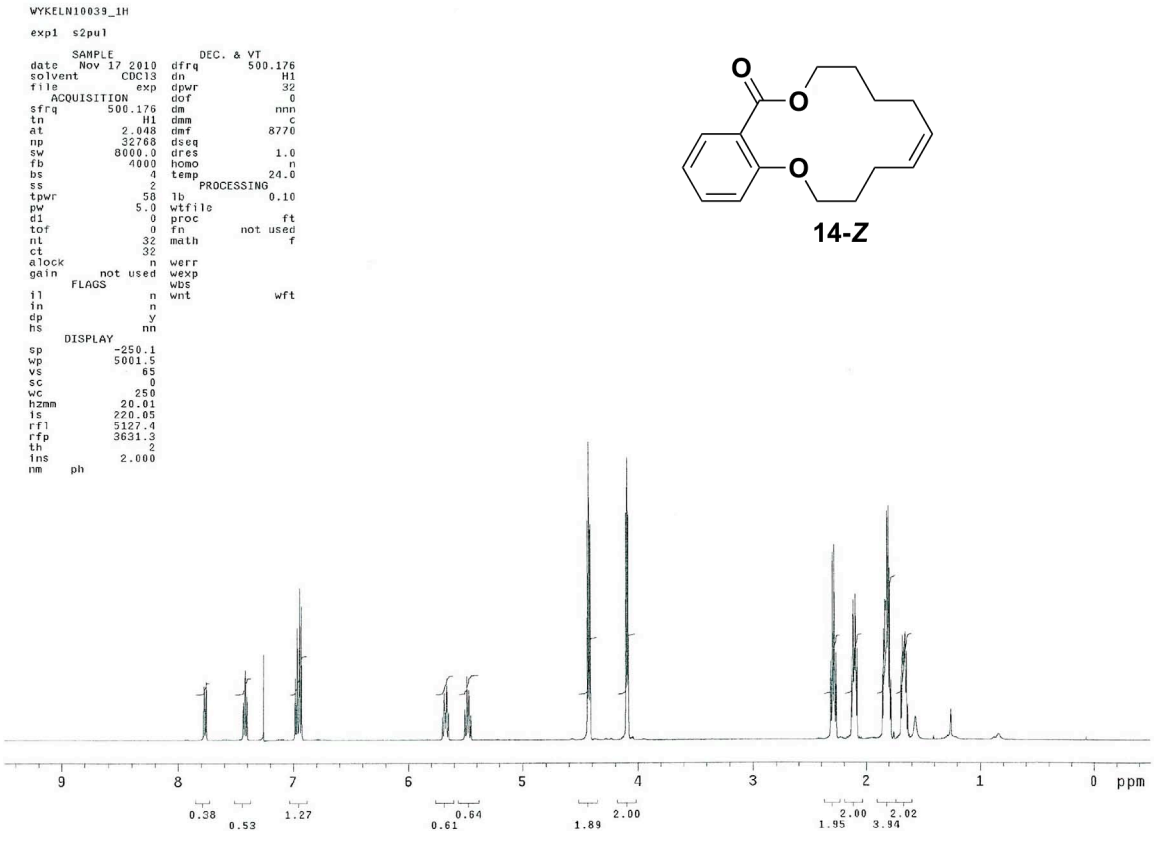

WYKELN8087_13C
exp3 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 836
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 37
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 1088.7
rfp 0
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)2Me
(±)
24'
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN10030_1H
exp1 s2pul
SAMPLE
date Apr 30 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN10030~
_1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 75
sc 0
wc 250
hzmm 19.99
is 359.36
rfl 4089.8
rfp 3629.1
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
(±)
24'
9
8
7
6
5
4
3
2
1
0
ppm
0.79
0.88
0.99
1.02
3.13
1.00
2.00
1.02
1.07
1.11
3.13
5.00
3.48
4.76
2.36


WYKELN10030_13C
exp3 s2pul
SAMPLE
date Apr 30 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 1632
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1086.9
wp 29995.3
vs 97
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10756.2
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)2Me
(±)
24'
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN16058_1H
exp2 s2pul
SAMPLE
date Feb 22 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500b/schreiber/WAN~
G/Pub2/WYKELN16058~
1H.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 288.14
rfl 5131.3
rfp 3631.3
th 2
ins 3.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Si(OEt)2Me
O
O
N
25
9
8
7
6
5
4
3
2
1
0
ppm
0.97 1.07 0.96 1.16 3.00 1.23 2.44 1.23 1.89
0.88 0.99 1.23 3.30 1.25 1.43 1.37 2.86

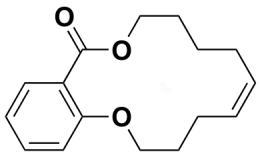

WYKELN16058_13C
exp2 s2pul
SAMPLE
date Feb 22 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500b/schreiber/WAN~
G/Pub2/WYKELN16058~
_13C.fid
ACQUISITION
sfrq 125.781
tn C13
at 1.170
np 65536
sw 28001.4
fb 15000
bs 16
tpwr 57
pw 8.0
d1 0.100
tof 0
nt 99999
ct 320
alock n
gain 56
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2086.2
wp 28000.5
vs 26
sc 0
wc 250
hzmm 112.00
is 500.00
rfl 11771.2
rfp 9684.2
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 15970
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Si(OEt)2Me
O
O
N
25
200
180
160
140
120
100
80
60
40
20
0
ppm


WYKELN10039_1H
exp1 s2pul
SAMPLE
date Nov 17 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 65
sc 0
wc 250
hzmm 20.01
is 220.05
rfl 5127.4
rfp 3631.3
th 2
ins 2.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 24.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
O
O
O
14-Z
9
8
7
6
5
4
3
2
1
0
ppm
0.38
0.53
1.27
0.61
0.64
1.89
2.00
1.95
2.00
3.94
2.02

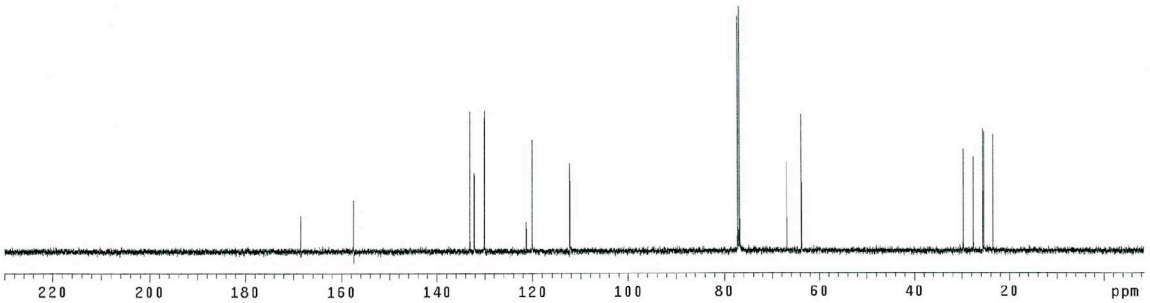
WYKELN10039_13C

exp4 s2pul

SAMPLE		DEC. & VT	
date	Nov 17 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	9180
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.8	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	1104	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1086.9	dpwr3	1
wp	29995.3	dof3	0
vs	54	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	5.10	dseq3	
is	500.00	dres3	1.0
rfl	10766.2	homo3	n
rfp	9678.3	PROCESSING	
th	3	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



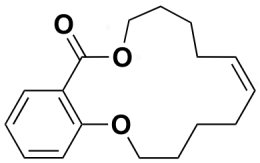
14-*Z*



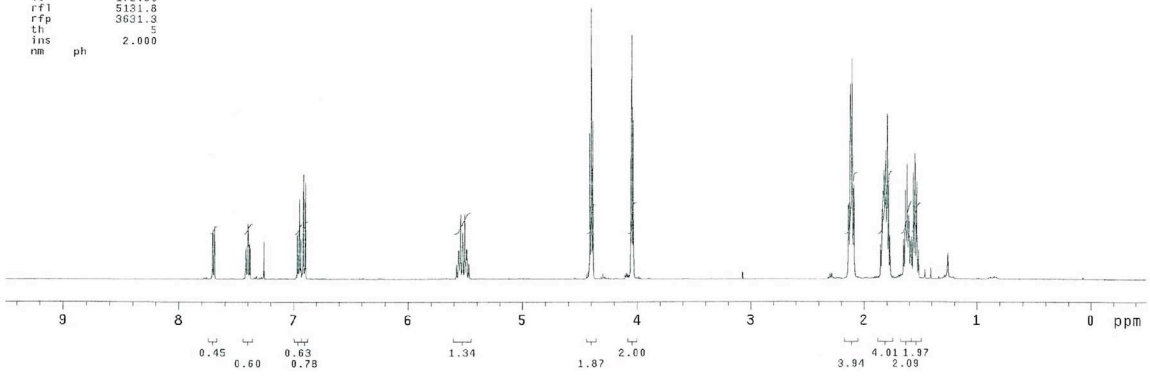
WYKELN10002_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 17 2010	dfrq	500.176
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	32
	ds2/vnmrsys/data/i~	dof	0
	500b/schreiber/WAN~	dm	nnn
	G/Pub1/WYKELN10002~	dmm	c
	1H.fid	dmf	8770
ACQUISITION		dseq	
sfrq	500.176	dres	1.0
tn	H1	homo	n
at	2.048	temp	24.0
np	32768	PROCESSING	
sw	8000.0	lb	0.10
fb	4000	wtfile	
bs	4	proc	ft
ss	2	fn	not used
tpwr	58	math	f
pw	5.0	werr	
d1	0	wexp	
tof	0	wbs	
nt	32	wnt	wft
ct	32		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5001.5		
vs	59		
sc	0		
wc	250		
hzmm	20.01		
is	173.80		
rfl	5131.8		
rfp	3031.3		
th	5		
ins	2.000		
nm	ph		



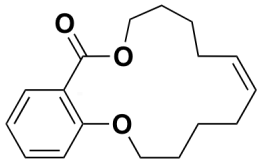
42-*Z*



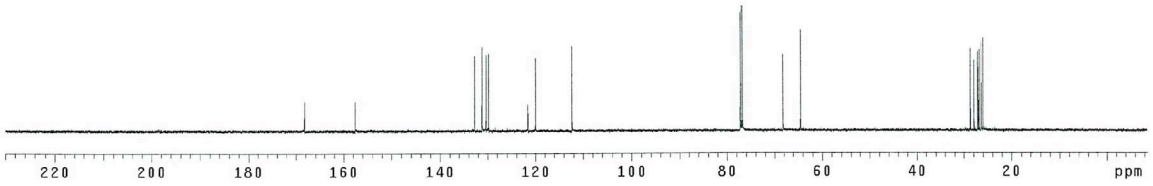
WYKELN10002_13C

exp3 s2pul

SAMPLE		DEC. & VT	
date	Nov 17 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	9180
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.8	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	999999	dof2	0
ct	1440	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1088.7	dpwr3	1
wp	29995.3	dof3	0
vs	27	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.0	homo3	n
rfp	9670.3	PROCESSING	
th	4	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



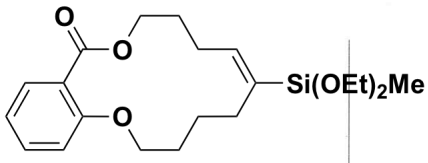
42-*Z*



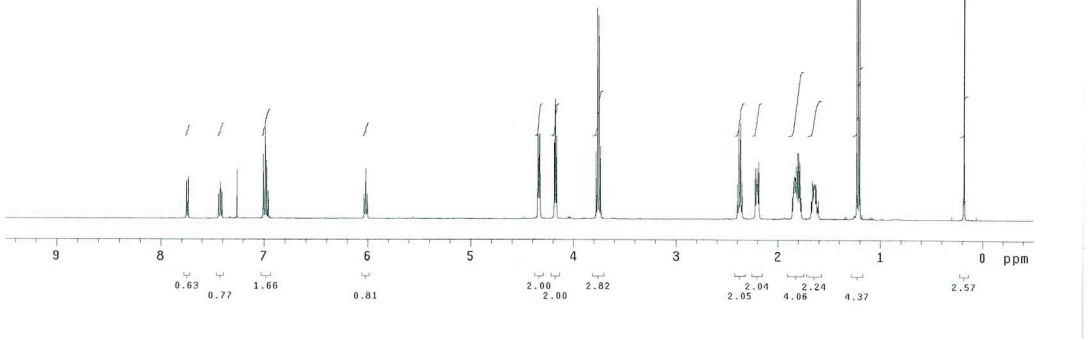
WYKELN16104_1H

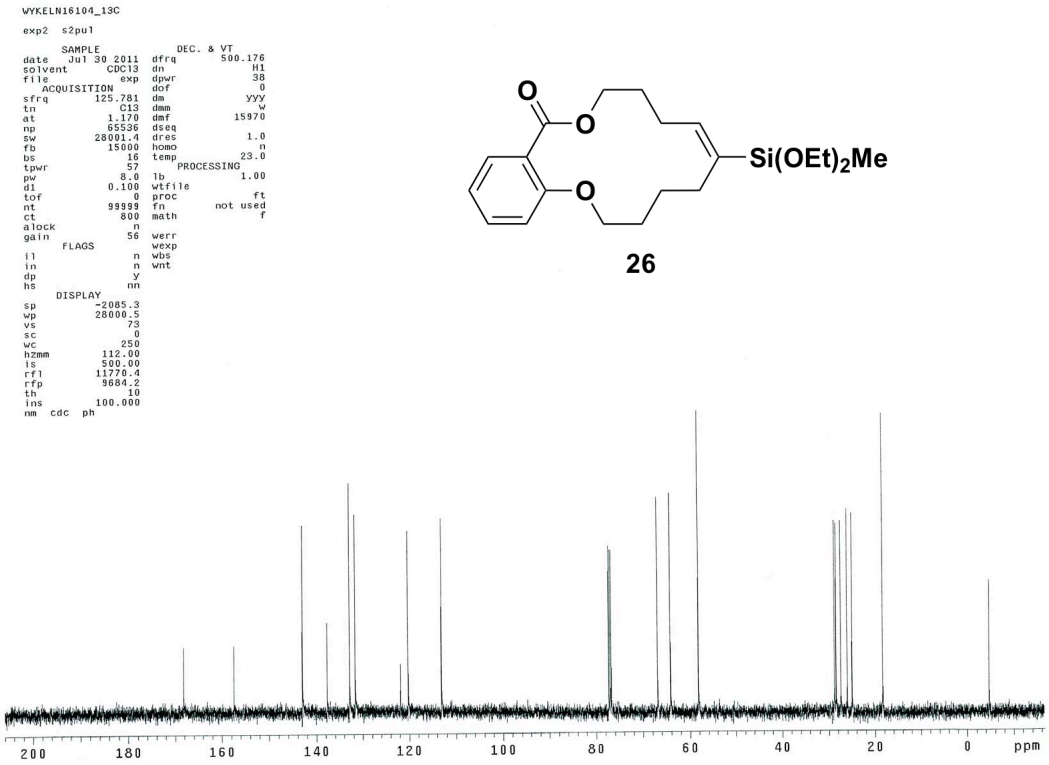
exp1 s2pul

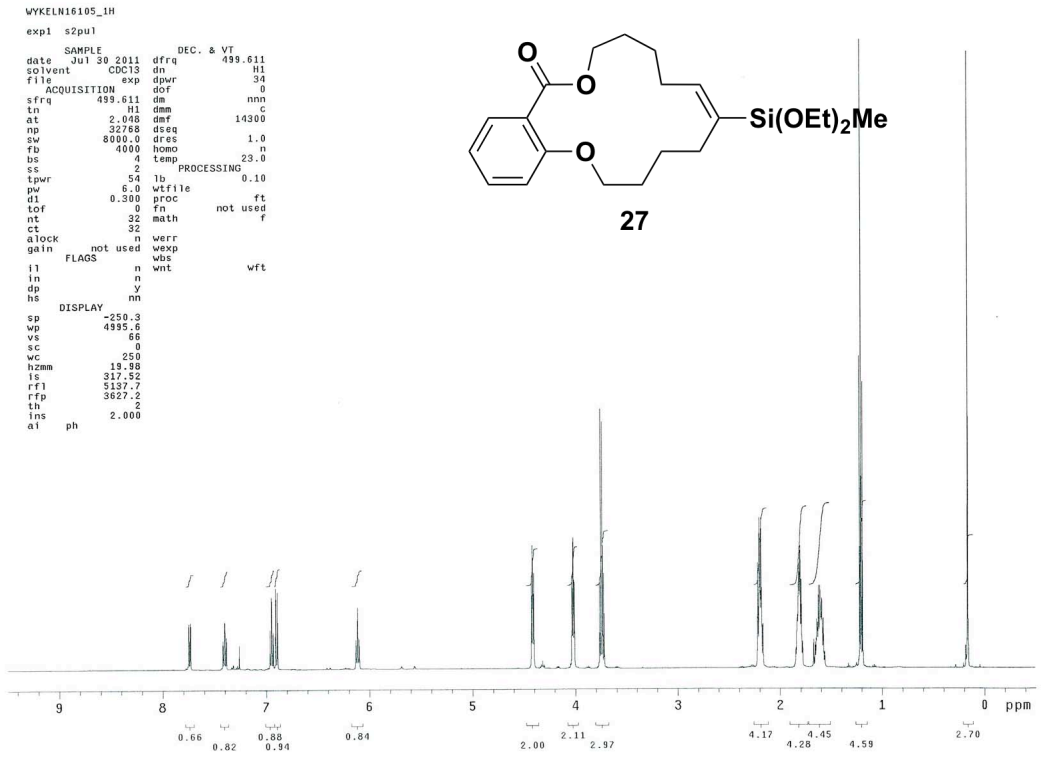
SAMPLE		DEC. & VT	
date	Jul 30 2011	dfrq	499.611
solvent	CDCl3	dn	H1
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.611	dm	nnn
tn	H1	dmm	c
at	2.068	dmf	14300
np	32768	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs	4	temp	23.0
ss	2	PROCESSING	
tpwr	54	lb	0.10
pw	6.0	wtfile	
d1	0.300	proc	ft
tof	0	fn	not used
nt	32	math	f
ct	32	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.3		
wp	4995.6		
vs	54		
sc	0		
wc	250		
hzmm	19.98		
is	304.35		
rfl	5137.7		
rfp	3627.2		
th	2		
ins	2.000		
ai ph			

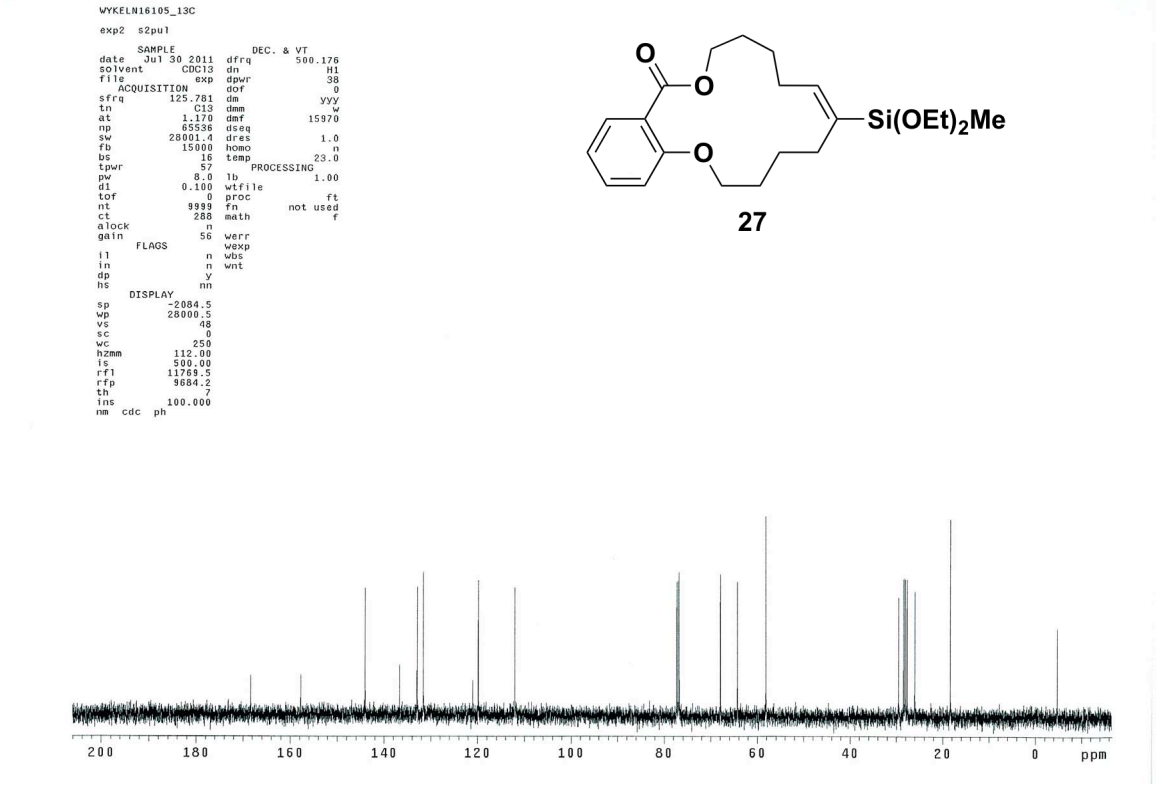


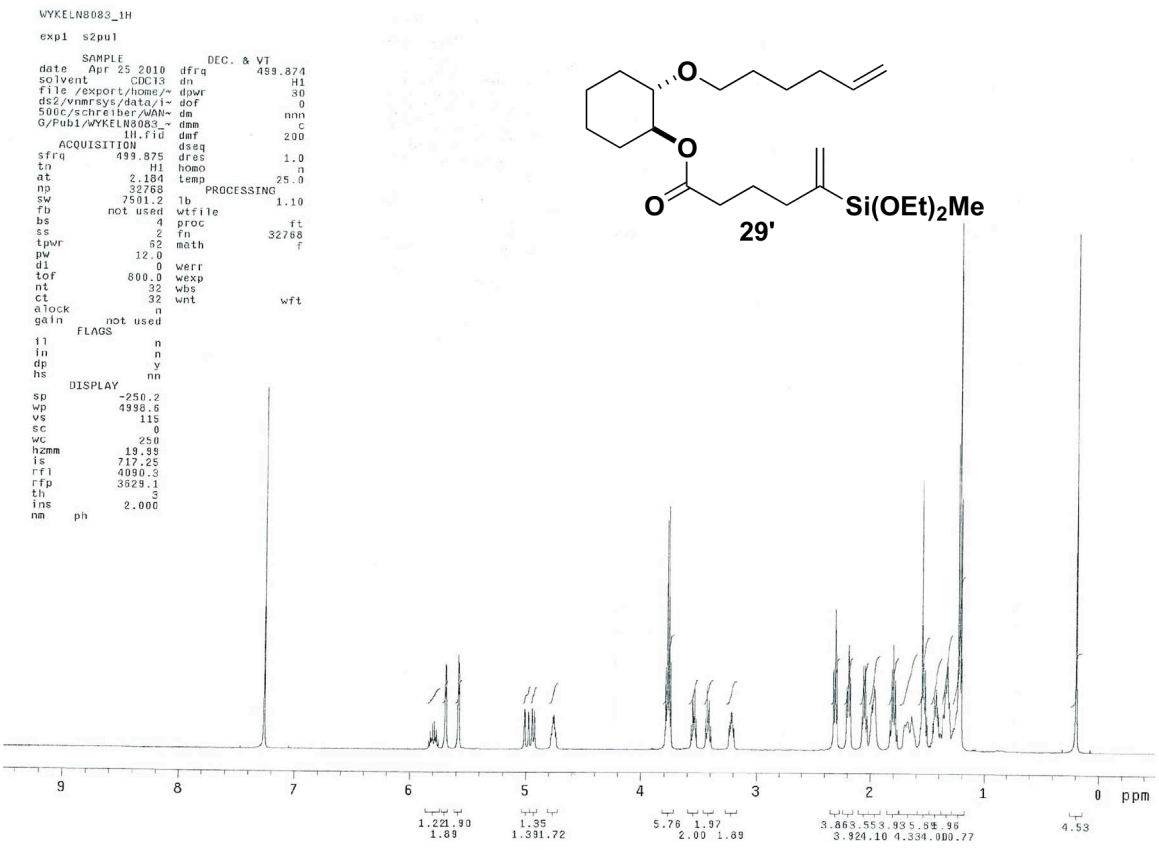
26

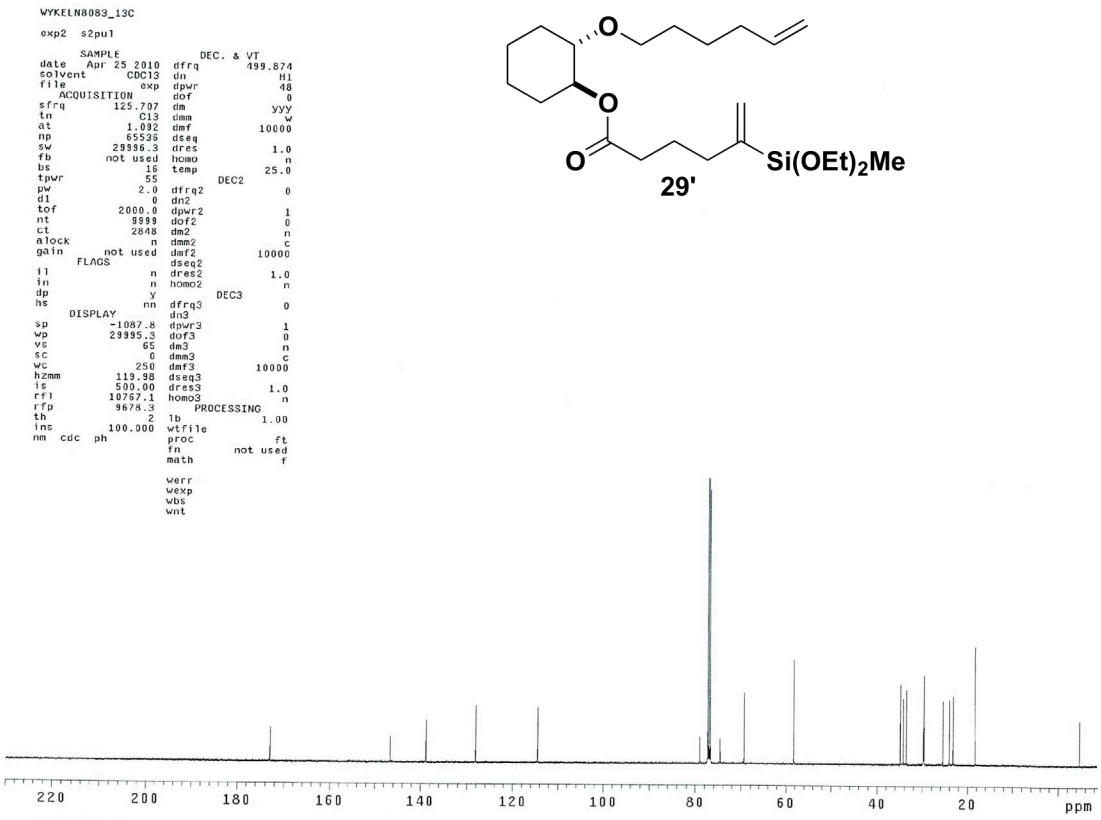


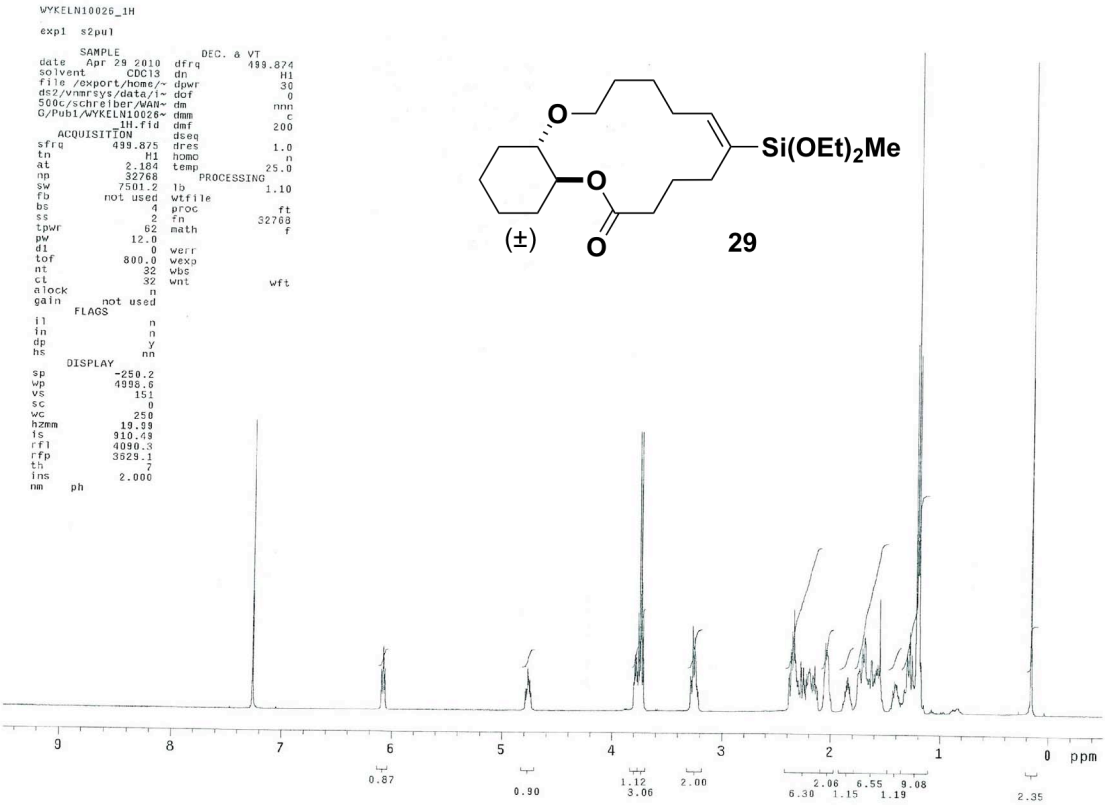

WYKELN16104_13C
exp2 s2pul
SAMPLE
date Jul 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.781
tn C13
at 1.170
np 65536
sw 28001.4
fb 15000
bs 16
tpwr 57
pw 8.0
d1 0.100
tof 0
nt 99999
ct 800
alock n
gain 56
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2085.3
wp 28000.5
vs 73
sc 0
wc 250
hzmm 112.00
is 500.00
rfl 11770.4
rfp 9684.2
th 10
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 15970
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)2Me
26
200
180
160
140
120
100
80
60
40
20
0
ppm

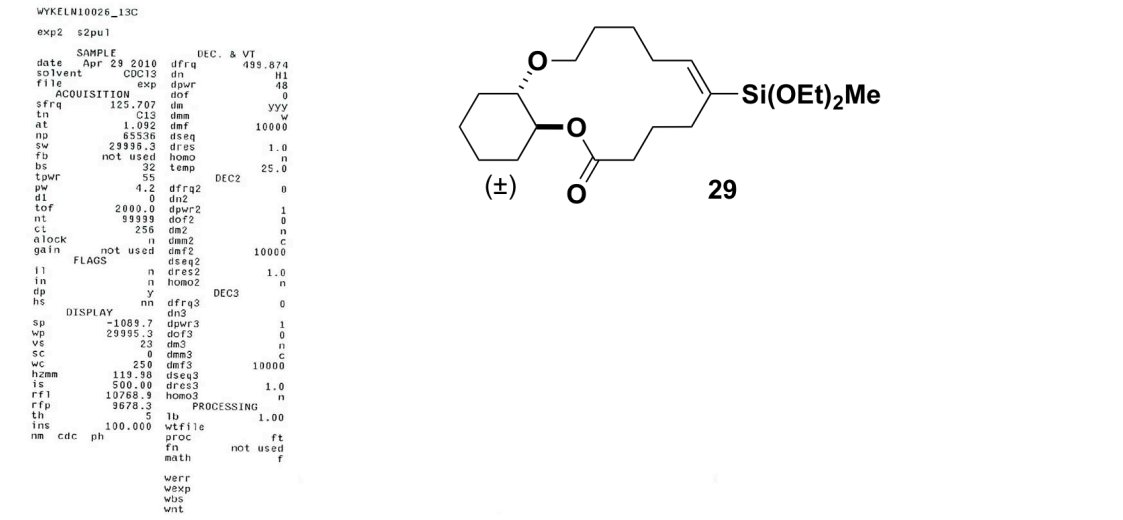

WYKELN16105_1H
exp1 s2pul
SAMPLE
date Jul 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.611
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 4995.6
vs 66
sc 0
wc 250
hzmm 19.98
is 317.52
rfl 5137.7
rfp 3627.2
th 2
ins 2.000
ai ph
DEC. & VT
dfrq 499.611
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 14300
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
27
9
8
7
6
5
4
3
2
1
0
ppm
0.66
0.82
0.88
0.94
0.84
2.00
2.11
2.97
4.17
4.28
4.45
4.59
2.70

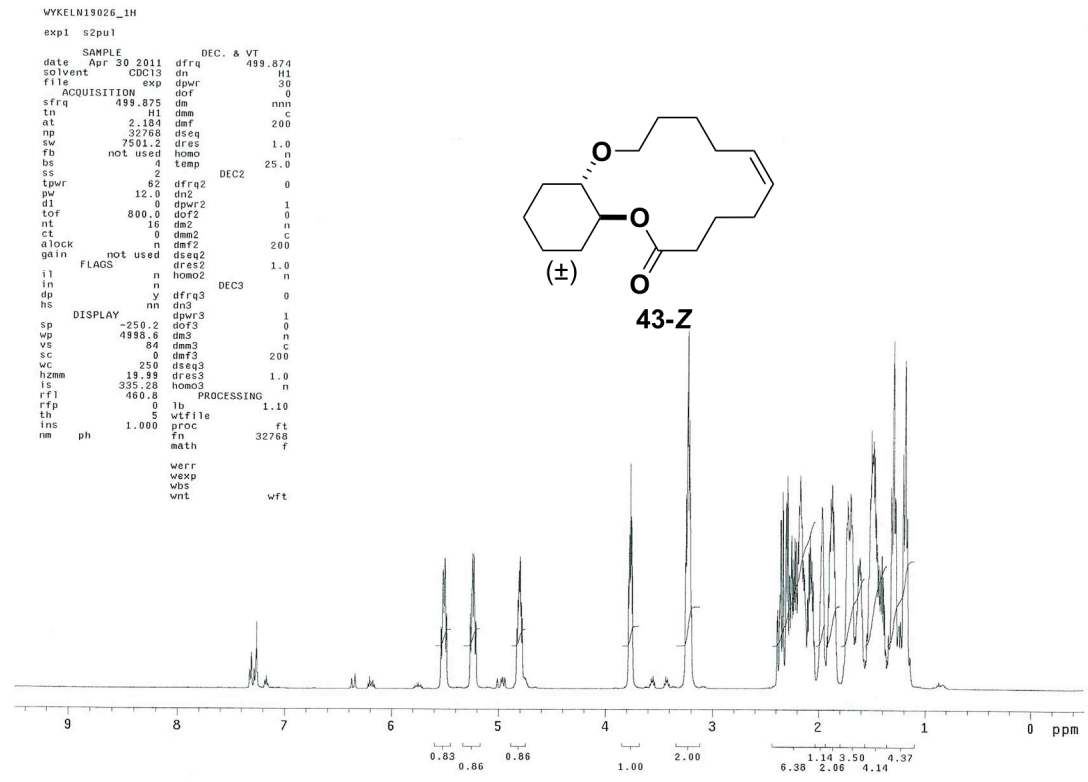

WYKELN16105_13C
exp2 s2pul
SAMPLE
date Jul 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.781
tn C13
at 1.170
np 65536
sw 28001.4
fb 15000
bs 16
tpwr 57
pw 8.0
d1 0.100
tof 0
nt 9999
ct 288
alock n
gain 56
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2084.5
wp 28000.5
vs 48
sc 0
wc 250
hzmm 112.00
is 500.00
rfl 11769.5
rfp 9684.2
th 7
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 15970
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)2Me
27
200
180
160
140
120
100
80
60
40
20
0
ppm

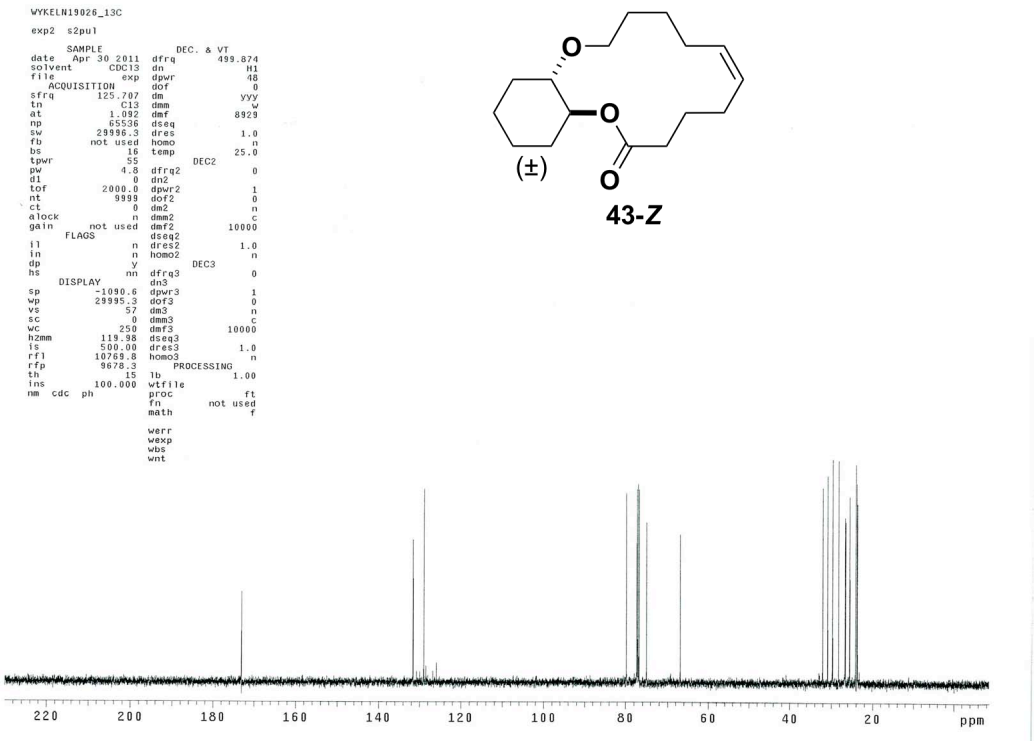

WYKELN8083_1H
exp1 s2pul
SAMPLE
date Apr 25 2010
solvent CDCl3
file /export/home/~ds2/vnmrsys/data/1~500c/schreiber/WAN~G/Pub1/WYKELN8083_~1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 52
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 115
sc 0
wc 250
hzmm 19.99
is 717.25
rfl 4090.3
rfp 3629.1
th 3
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
29'
9
8
7
6
5
4
3
2
1
0
ppm
1.22 1.90
1.89
1.35
1.39 1.72
5.76 1.97
2.00 1.89
3.86 3.55 3.93 5.59 1.96
3.92 4.10 4.33 4.00 0.77
4.53

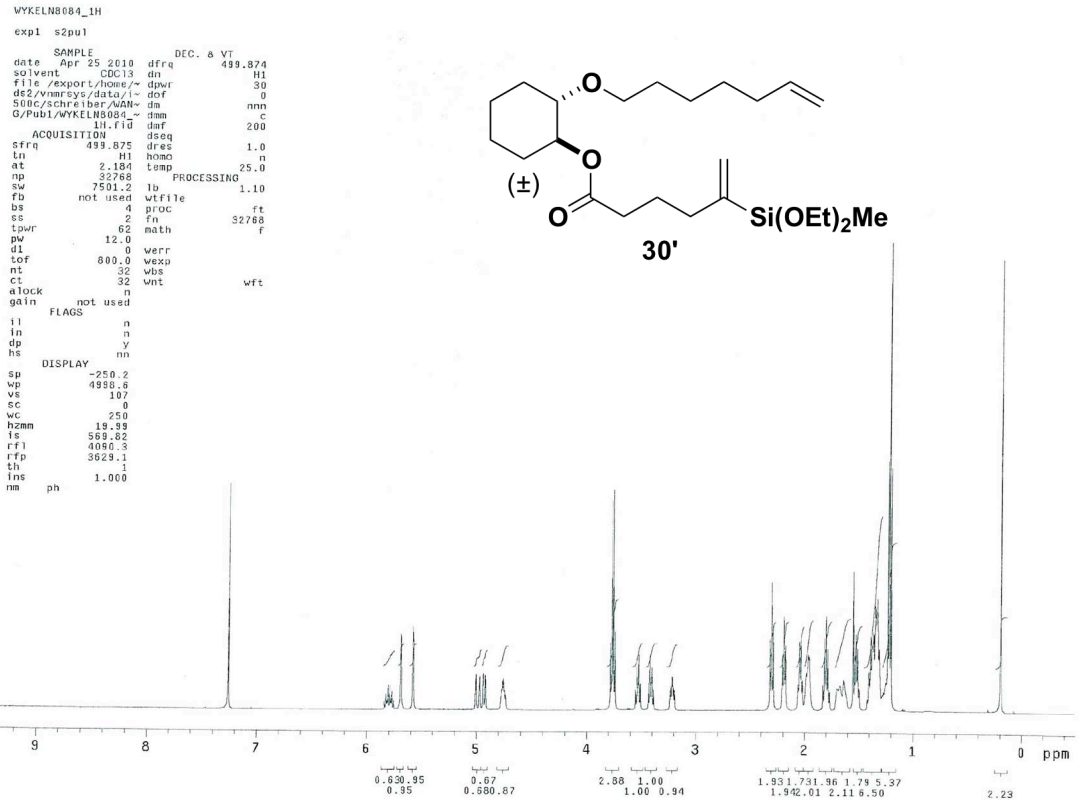

WYKELN8083_13C
exp2 s2pul
SAMPLE
date Apr 25 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 2.0
d1 0
tof 2000.0
nt 9888
ct 2848
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 65
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
Si(OEt)2Me
29'
220
200
180
160
140
120
100
80
60
40
20
ppm

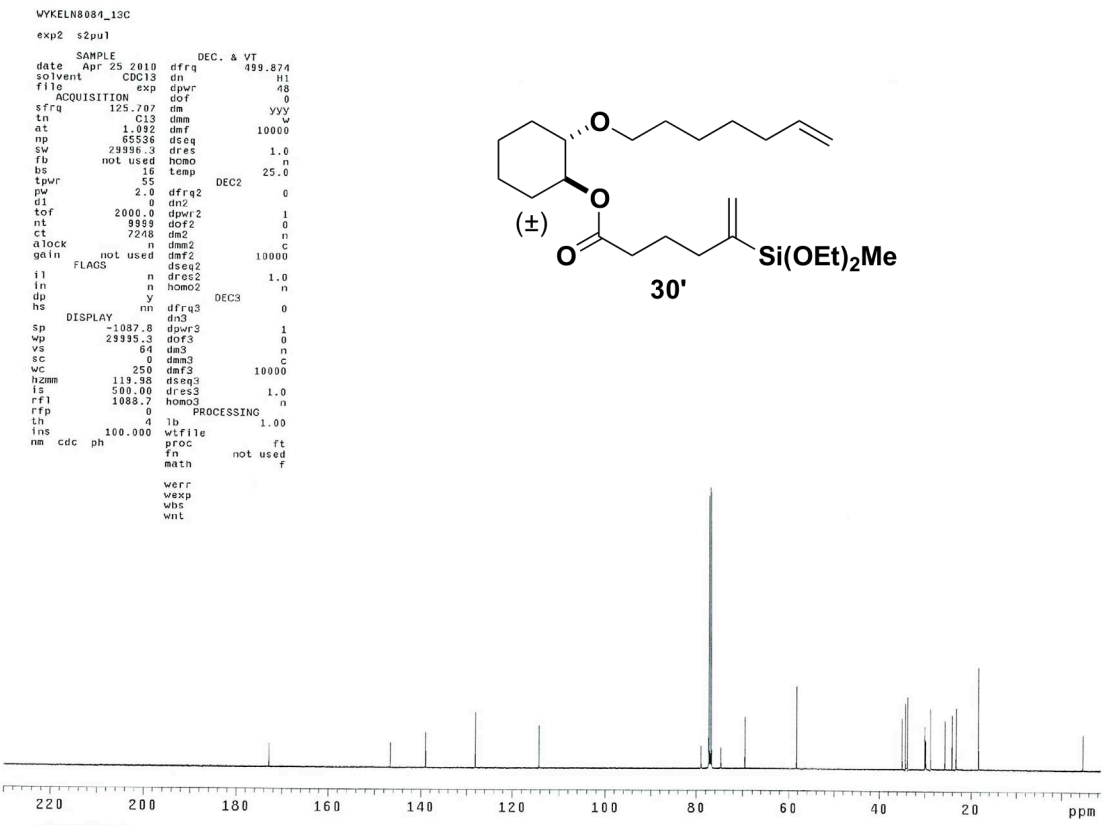

WYKELN10026_1H
exp1 s2pul
SAMPLE
date Apr 29 2010
solvent CDCl3
file /export/home/~
de2/vnmrsys/data/i~
500c/schreiber/WAR~
G/Pub1/WYKELN10026~
_1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 910.49
rfl 4090.3
rfp 3529.1
th 7
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
(±)
29
9
8
7
6
5
4
3
2
1
0
ppm
0.87
0.90
1.12
3.06
2.00
2.06
6.30
6.55
1.15
9.08
1.19
2.35

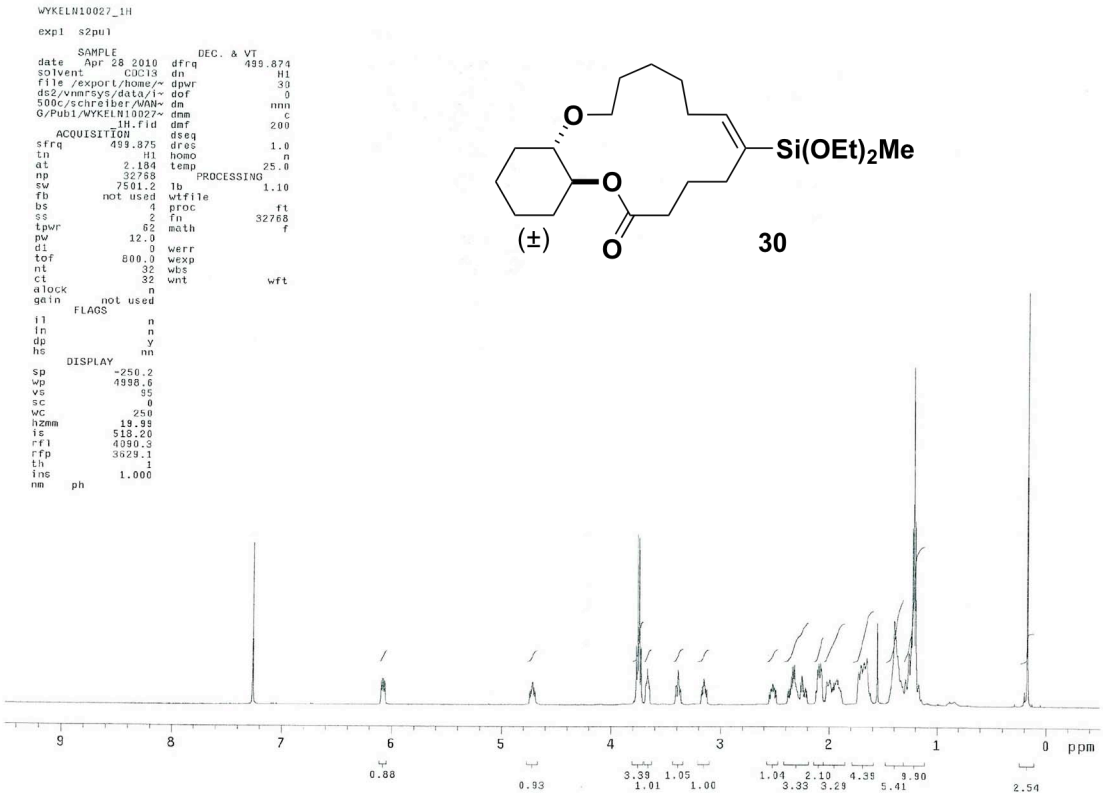

WYKELN10026_13C
exp2 s2pul
SAMPLE
date Apr 29 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 256
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1089.7
wp 29995.3
vs 23
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.9
rfp 9678.3
th 5
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
Si(OEt)2Me
29
220
200
180
160
140
120
100
80
60
40
20
ppm

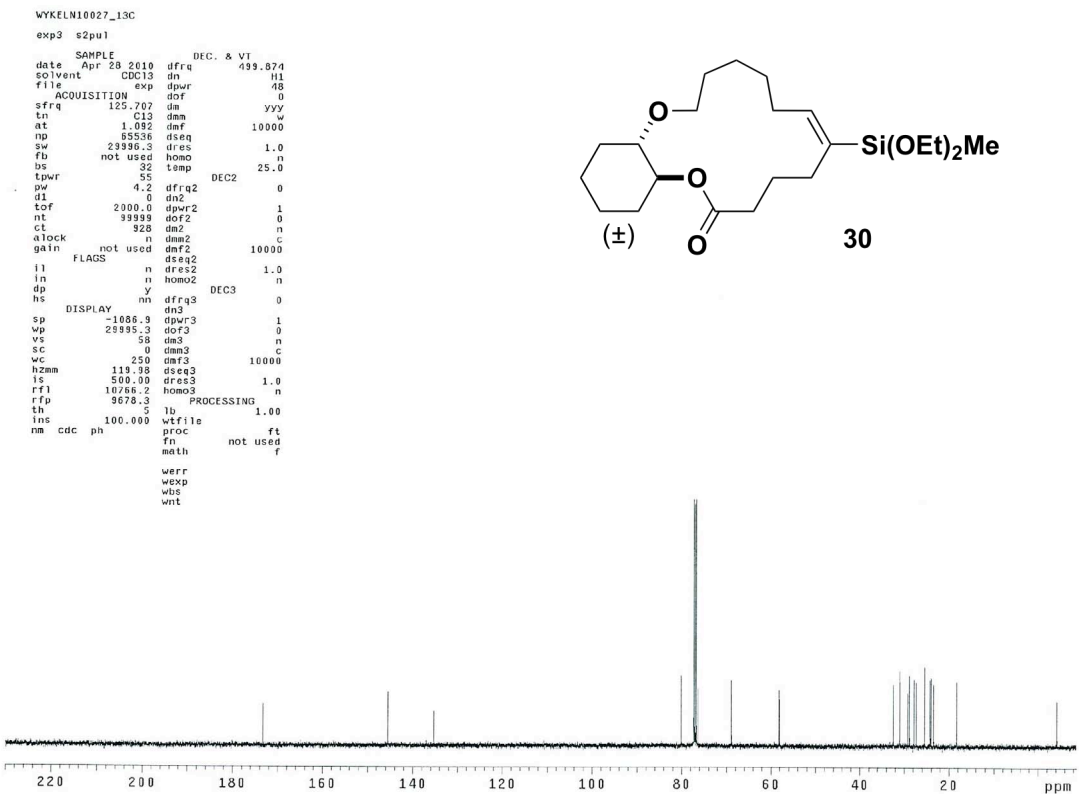

WYKELN19026_1H
exp1 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 84
sc 0
wc 250
hzmm 19.99
is 335.28
rfl 460.8
rfp 0
th 5
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
(±)
43-Z
9
8
7
6
5
4
3
2
1
0 ppm
0.83
0.86
0.86
1.00
2.00
1.14 3.50 4.37
6.38 2.06 4.14

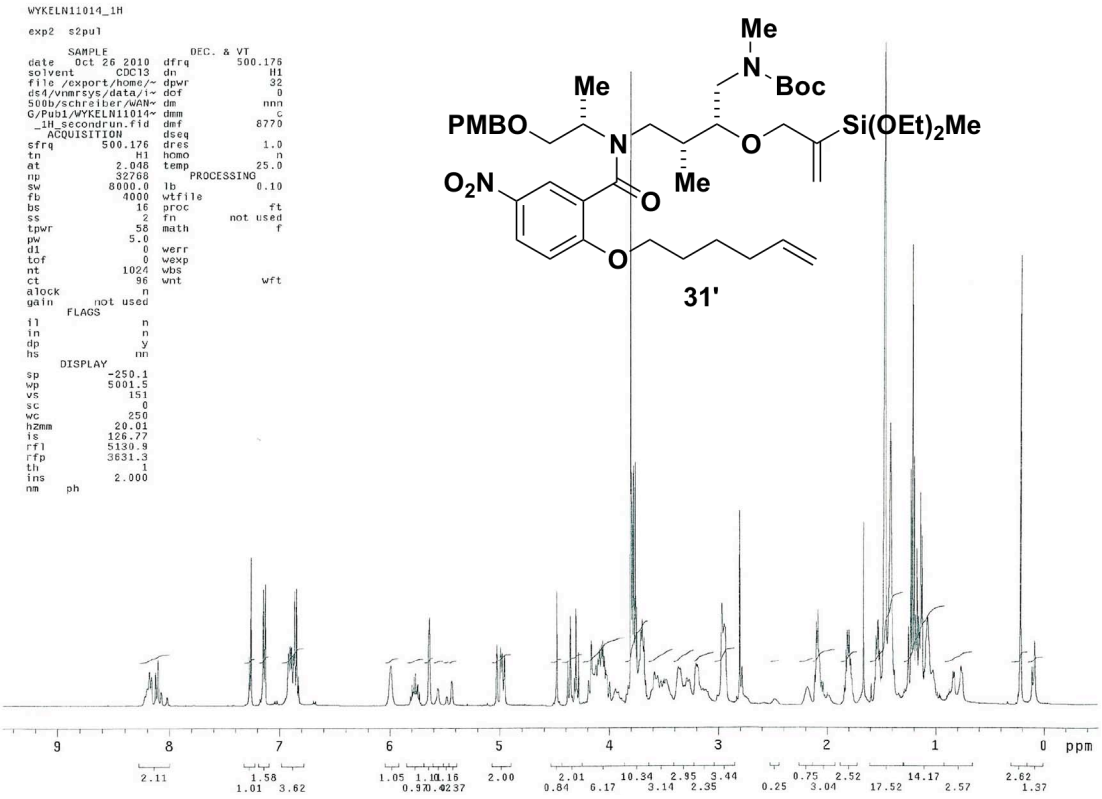

WYKELN19026_13C
exp2 s2pul
SAMPLE
date Apr 30 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1090.6
wp 29995.3
vs 57
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10769.8
rfp 9678.3
th 15
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
43-Z
220
200
180
160
140
120
100
80
60
40
20
ppm

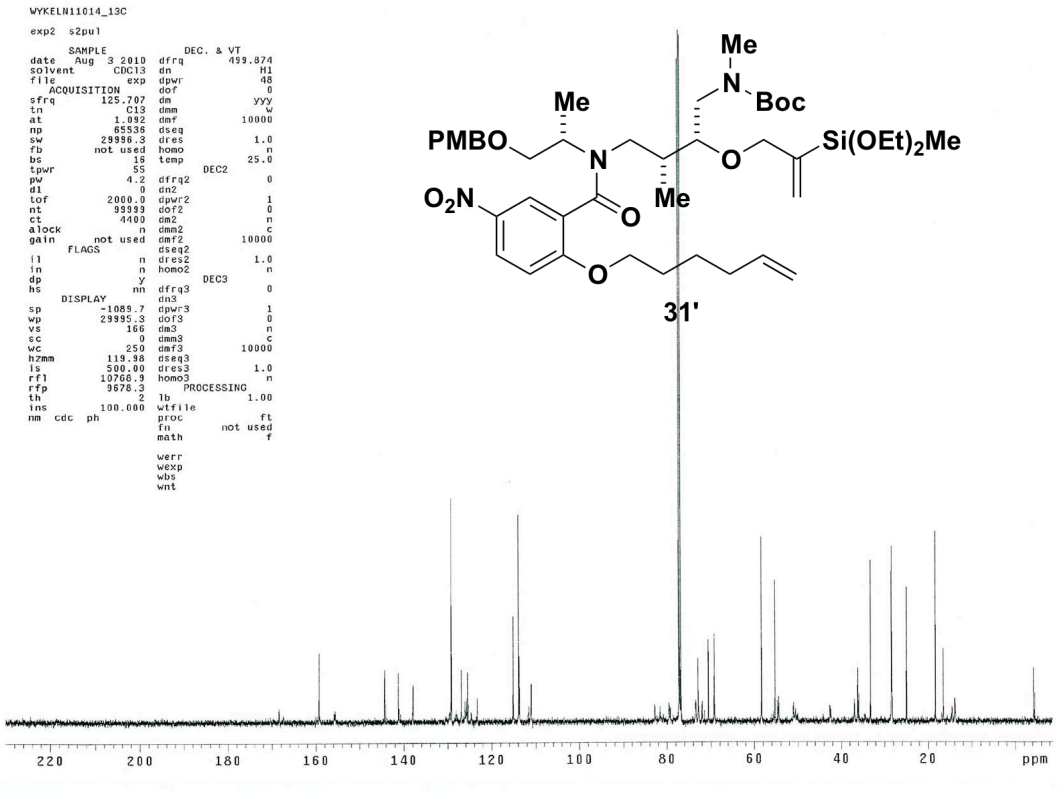

WYKELN8084_1H
exp1 s2pul
SAMPLE
date Apr 25 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Publ/WYKELN8084_~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 107
sc 0
wc 250
hzmm 19.99
is 569.82
rfl 4090.3
rfp 3629.1
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
(±)
Si(OEt)2Me
30'
9
8
7
6
5
4
3
2
1
0 ppm
0.630.95
0.95
0.67
0.680.87
2.88 1.00
1.00 0.94
1.931.731.96 1.79 5.37
1.942.01 2.11 6.50
2.23

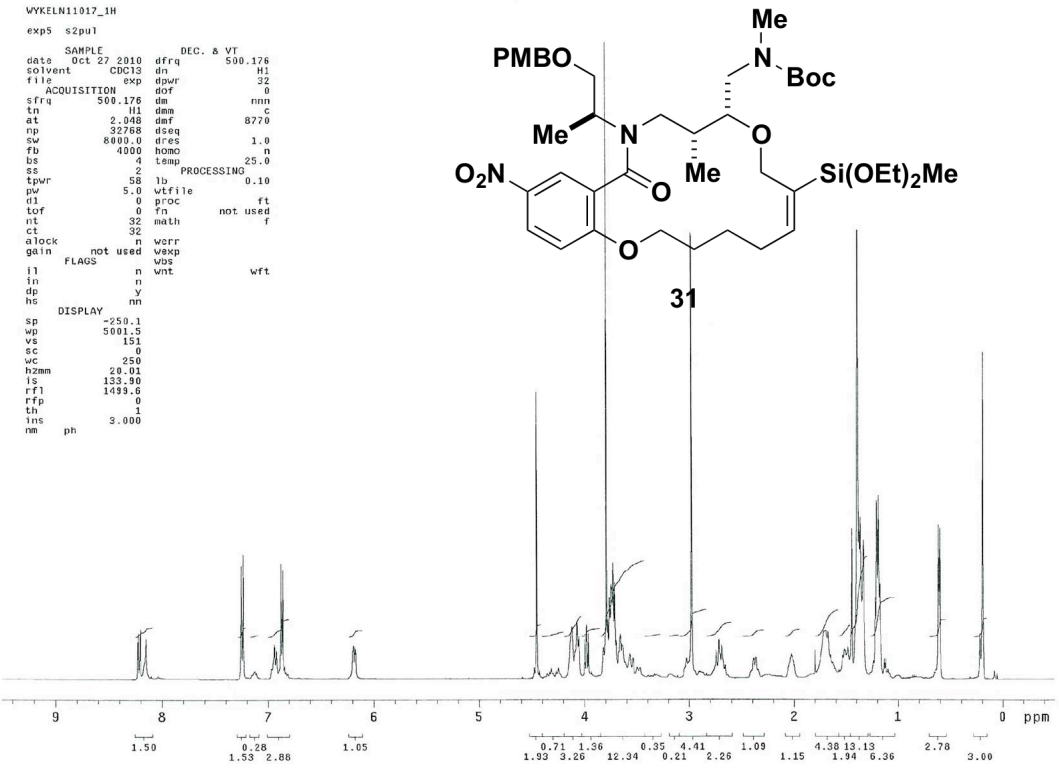

WYKELN8084_13C
exp2 s2pul
SAMPLE
date Apr 25 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 2.0
d1 0
tof 2000.0
nt 9999
ct 7248
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 64
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 1088.7
rfp 0
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
(±)
O
Si(OEt)2Me
30'
220
200
180
160
140
120
100
80
60
40
20
ppm

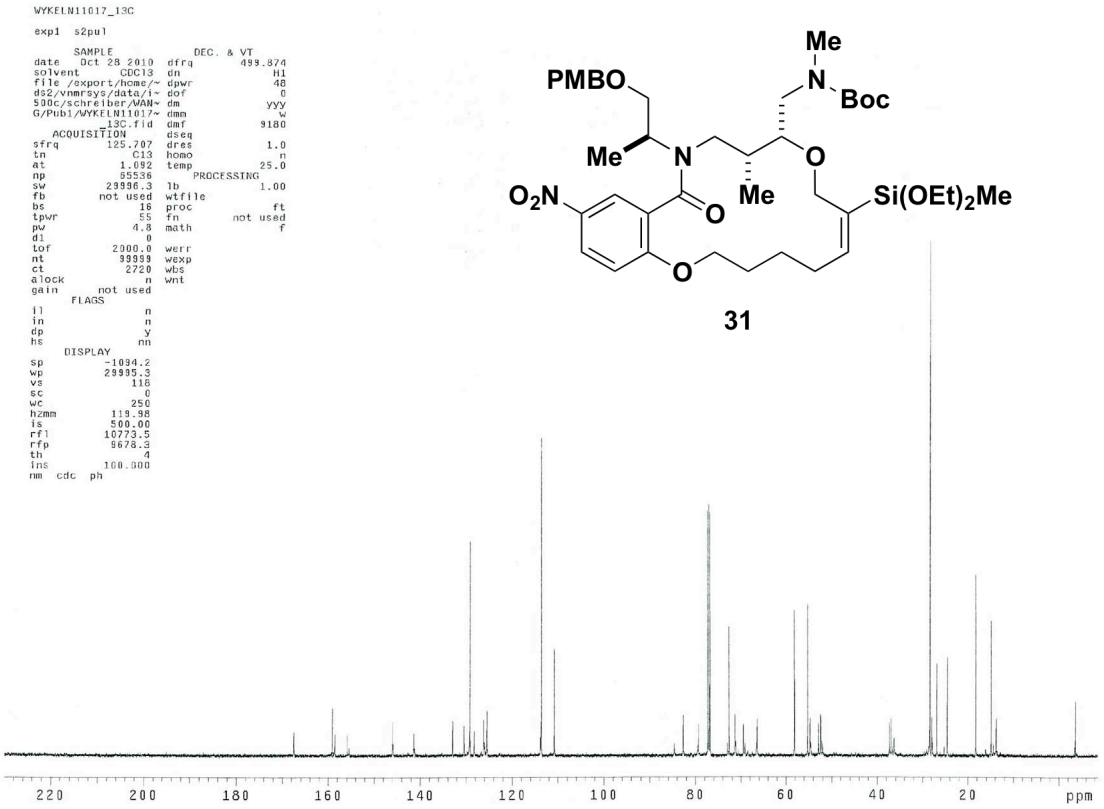

WYKELN10027_1H
exp1 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN10027~
_1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 95
sc 0
wc 250
hzmm 19.99
is 518.20
rfl 4090.3
rfp 3629.1
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.8
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
Si(OEt)2Me
(±)
30
9
8
7
6
5
4
3
2
1
0
ppm
0.88
0.93
3.39
1.01
1.05
1.00
1.04
3.33
2.10
3.29
4.35
5.41
9.90
2.54

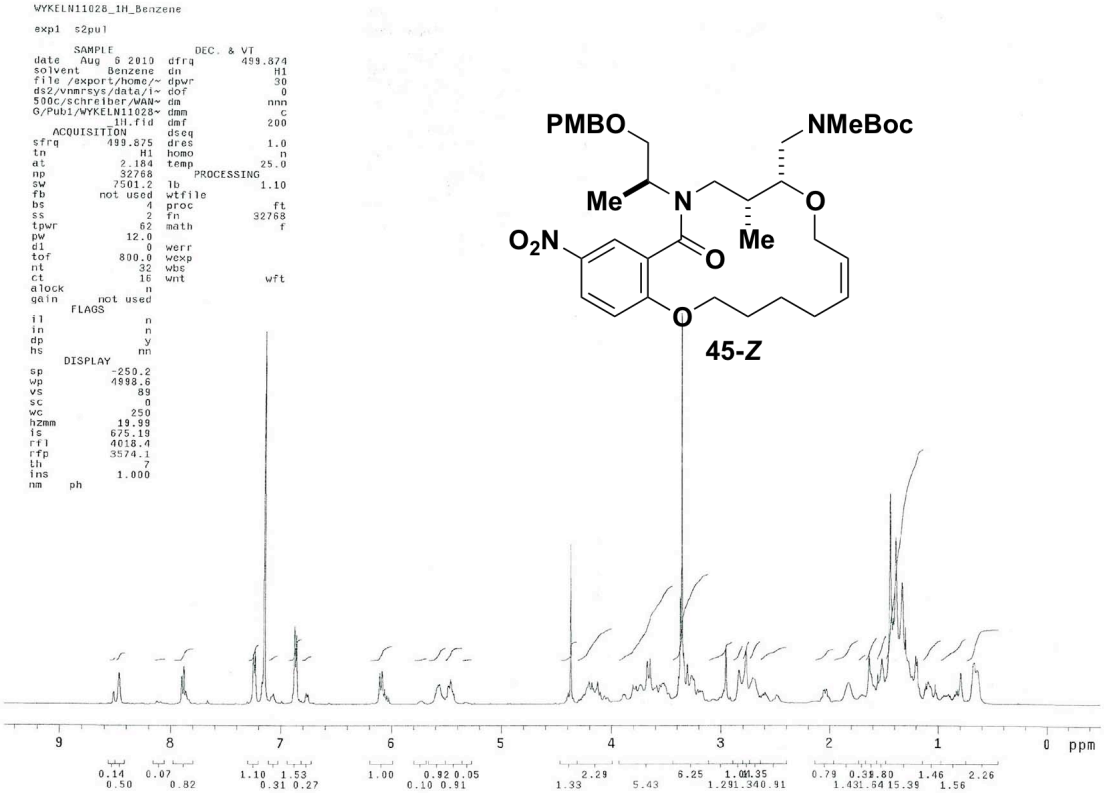

WYKELN10027_13C
exp3 s2pul
SAMPLE
date Apr 28 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 23980.8
fb not used
bs 32
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 928
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1086.9
wp 25935.3
vs 58
sc 0
wc 250
hzmm 119.98
is 500.00
rf1 10766.2
rfp 9678.3
th 5
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
Si(OEt)2Me
30
220
200
180
160
140
120
100
80
60
40
20
ppm

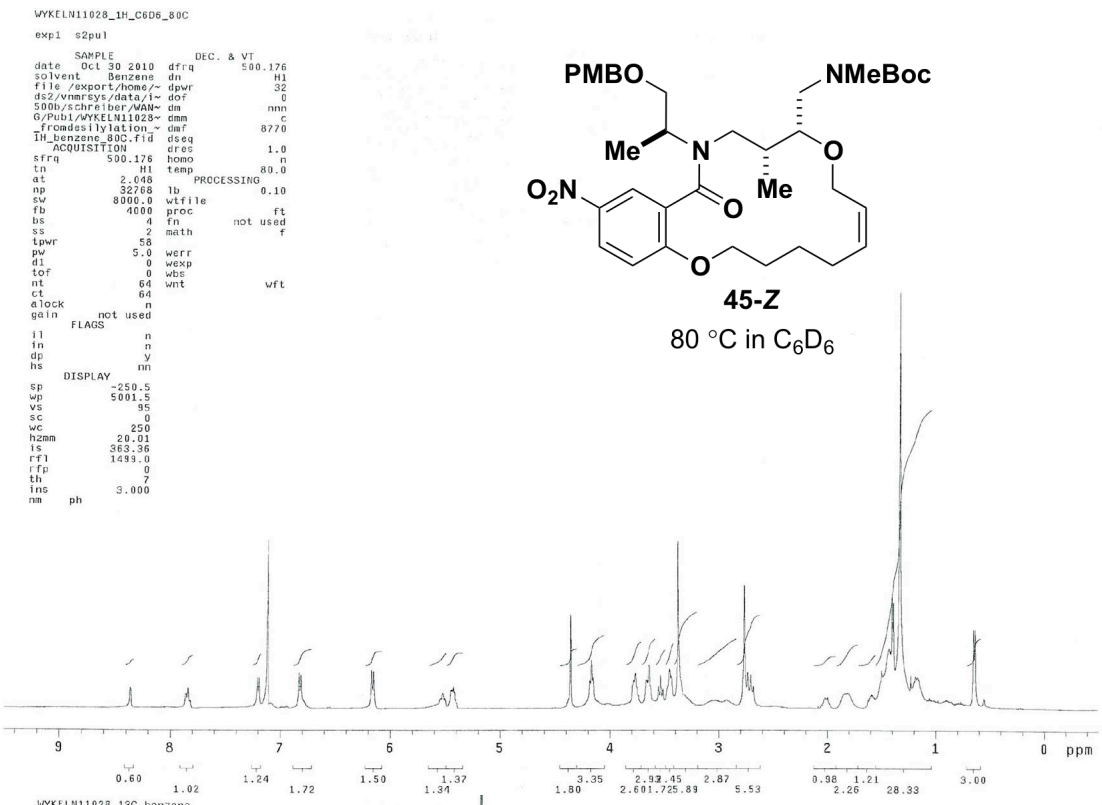

WYKELN11014_1H
exp2 s2pul
SAMPLE
date Oct 26 2010
solvent CDCl3
file /export/home/~
ds4/vnmrsys/data/1~
500b/schreiber/WAN~
G/Pub1/WYKELN11014~
_1H_secondrun.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.046
np 32768
sw 8000.0
fb 4000
bs 16
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 1024
ct 96
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 126.77
rf1 5130.8
rfp 3631.3
th 1
ins 2.000
nm ph
DEC. & VT
dfrq 500.175
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Me
N
Boc
Me
PMBO
N
O
Si(OEt)2Me
O2N
O
Me
O
31'
9
8
7
6
5
4
3
2
1
0
ppm
2.11
1.58
1.01 3.62
1.05 1.10 1.16
0.97 0.42 37
2.00
2.01
0.84 6.17
10.34
3.14
2.95
2.35
3.44
0.25
0.75
3.04
2.52
14.17
17.52
2.57
2.62
1.37

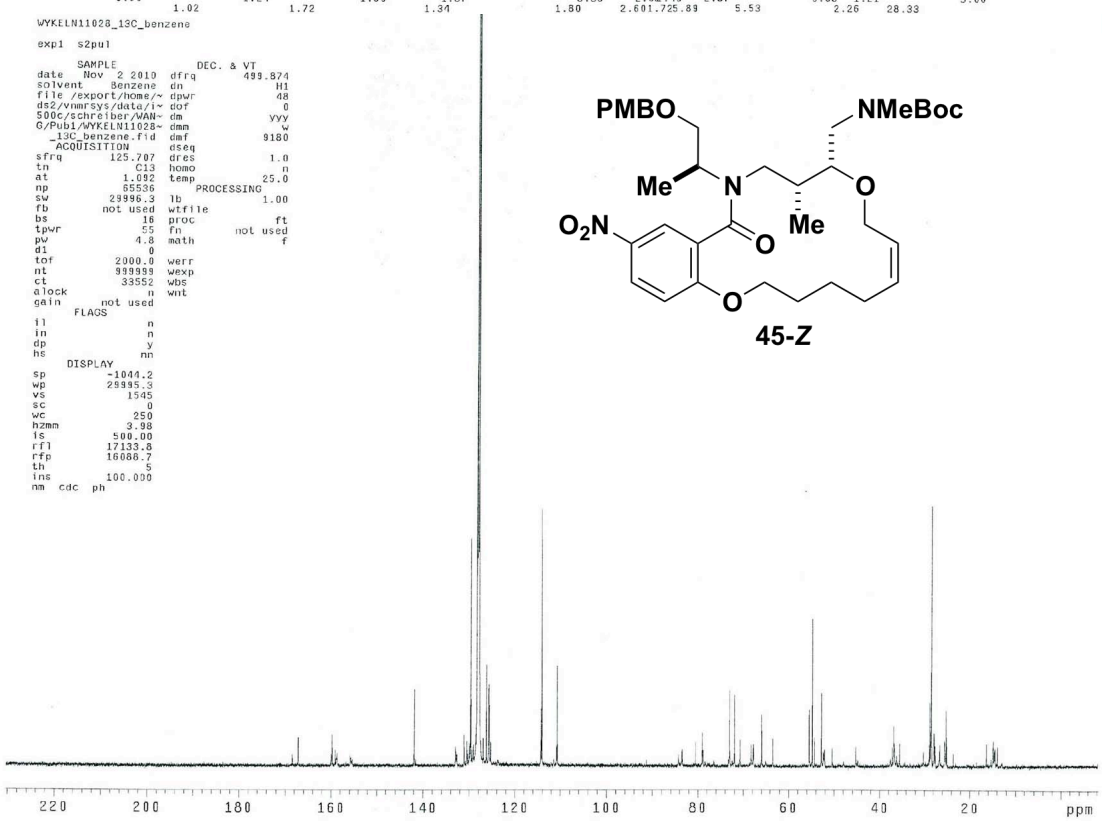

WYKELN11014_13C
exp2 s2pul
SAMPLE
date Aug 3 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 4400
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1089.7
wp 29995.3
vs 166
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.9
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Me
N
Boc
PMBO
Me
N
O
Si(OEt)2Me
O2N
O
Me
O
31'
220
200
180
160
140
120
100
80
60
40
20
ppm

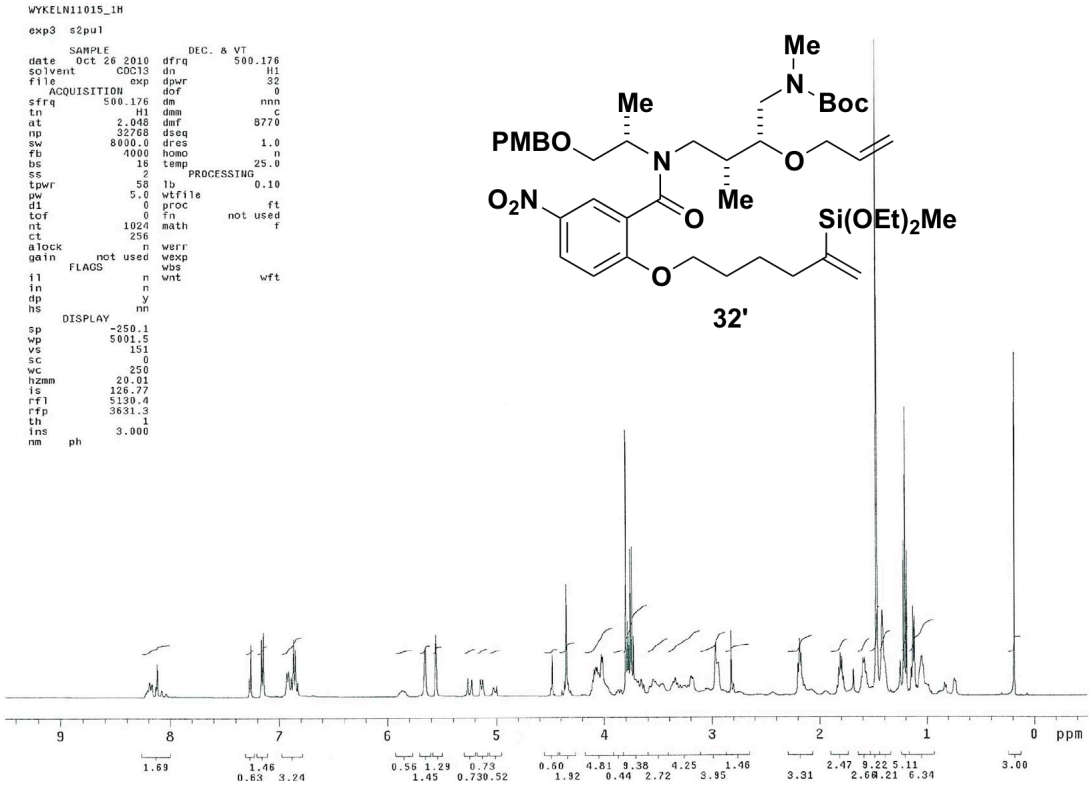

WYKELN11017_1H
exp5 s2pul
SAMPLE
date Oct 27 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 133.90
rfl 1499.6
rfp 0
th 1
ins 3.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Me
N
Boc
PMBO
Me
N
O
O2N
O
Me
Si(OEt)2Me
O
31
9
8
7
6
5
4
3
2
1
0
ppm
1.50
0.28
1.53 2.88
1.05
0.71 1.36
1.93 3.26 12.94
0.35
0.21 4.41 2.26
1.09
1.15
4.38 13.13
1.94 6.36
2.78
3.00

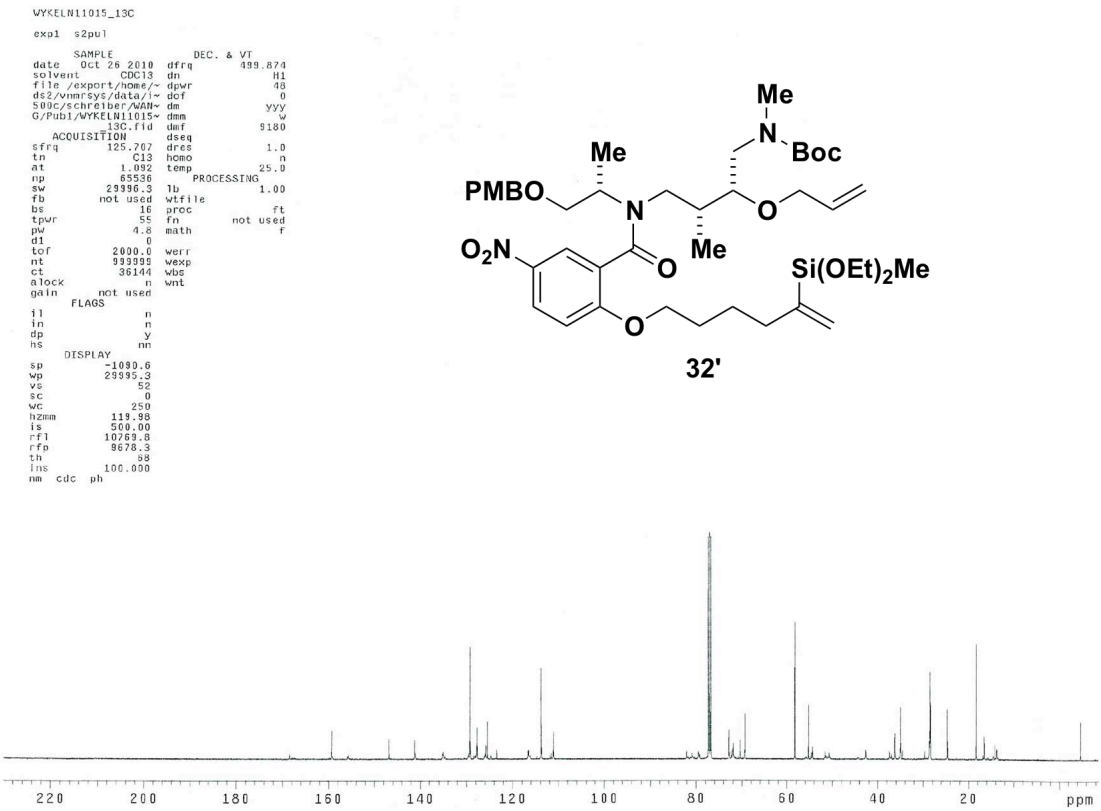

WYKELN11017_13C
exp1 s2pul
SAMPLE
date Oct 28 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN11017~
_13C.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 55536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
dl 0
tof 2000.0
nt 99999
ct 2720
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1094.2
wp 29995.3
vs 118
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10723.5
rfp 9678.3
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 9180
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
PMBO
Me
N
Boc
Me
N
O
O2N
O
Me
O
Si(OEt)2Me
31
220
200
180
160
140
120
100
80
60
40
20
ppm

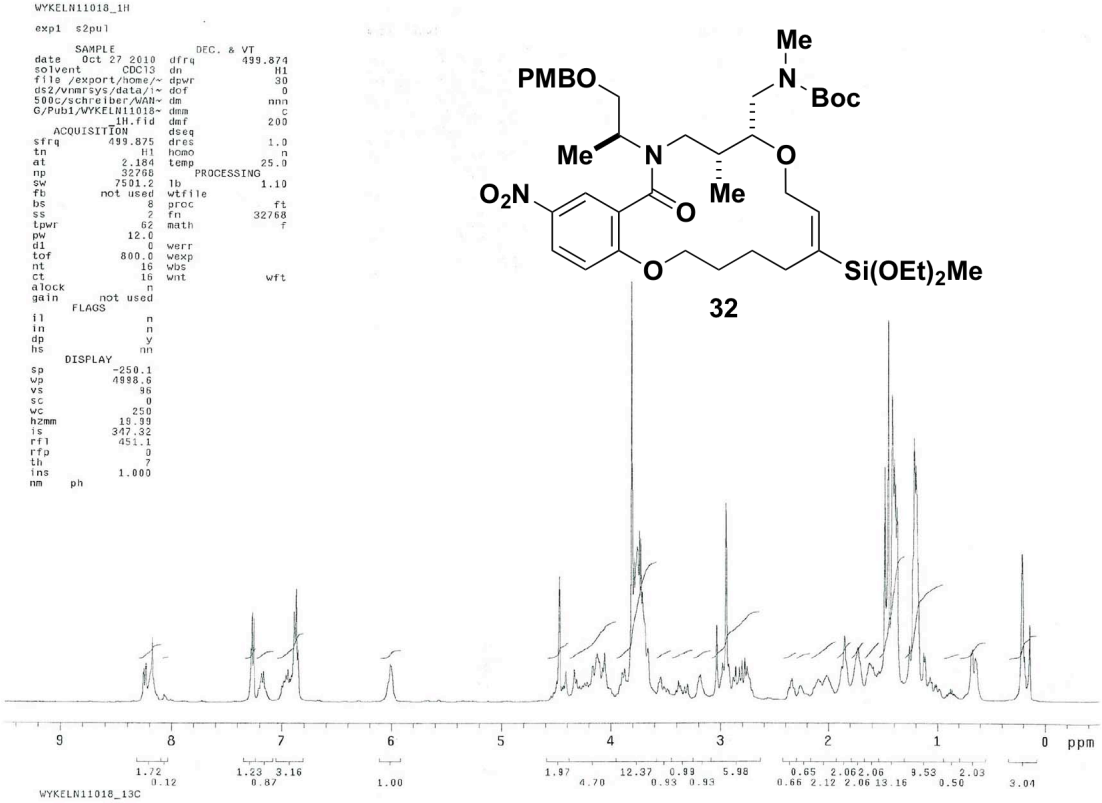

WYKELN11028_1H_Benzene
exp1 s2pul
SAMPLE
date Aug 6 2010
solvent Benzene
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN11028~
_1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
dl 0
tof 800.0
nt 32
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 89
sc 0
wc 250
hzmm 19.99
is 675.19
rfl 4018.4
rfp 3574.1
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
PMBO
NMeBoc
Me
N
O
O2N
O
Me
O
45-Z
9
8
7
6
5
4
3
2
1
0 ppm
0.14 0.07 1.10 1.53 1.00 0.92 0.05 2.29 6.25 1.01 1.35 0.79 0.31 1.80 1.46 2.26
0.50 0.82 0.31 0.27 0.10 0.91 1.33 5.43 1.29 1.34 0.91 1.43 1.54 15.39 1.56

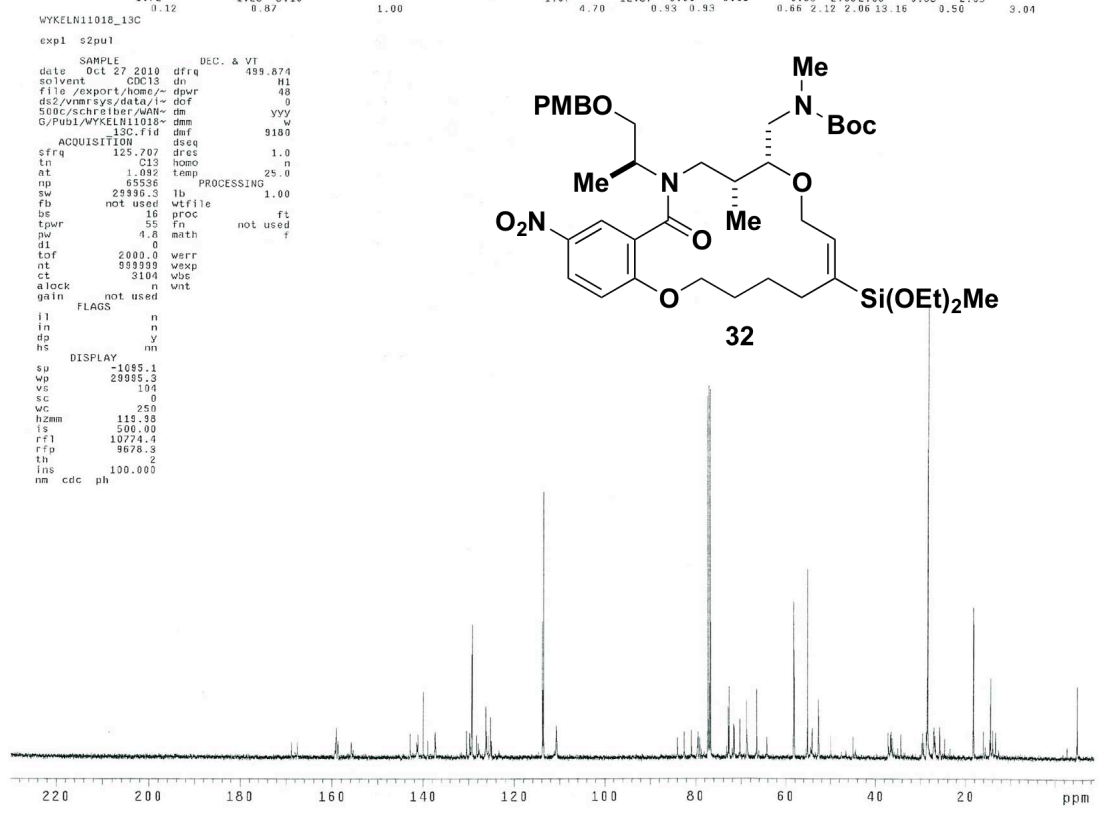

WYKELN11028_1H_C6D6_80C
exp1 s2pul
SAMPLE
date Oct 30 2010
solvent Benzene
file /export/home/~
ds2/vnmrsys/data/i~
500b/schreiber/WAN~
G/Pub1/WYKELN11028~
fromdesilylation~
1H_benzene_80C.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.5
wp 5001.5
vs 95
sc 0
wc 250
hzmm 20.01
is 363.36
rfl 1499.0
rfp 0
th 7
ins 3.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 80.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
PMBO
NMeBoc
Me
N
O
Me
O2N
O
O
45-Z
80 °C in C6D6
9
8
7
6
5
4
3
2
1
0 ppm
0.60
1.02
1.24
1.72
1.50
1.37
1.34
3.35
1.80
2.93
2.45
2.87
2.60
1.72
5.89
5.53
0.98
2.26
1.21
28.33
3.00

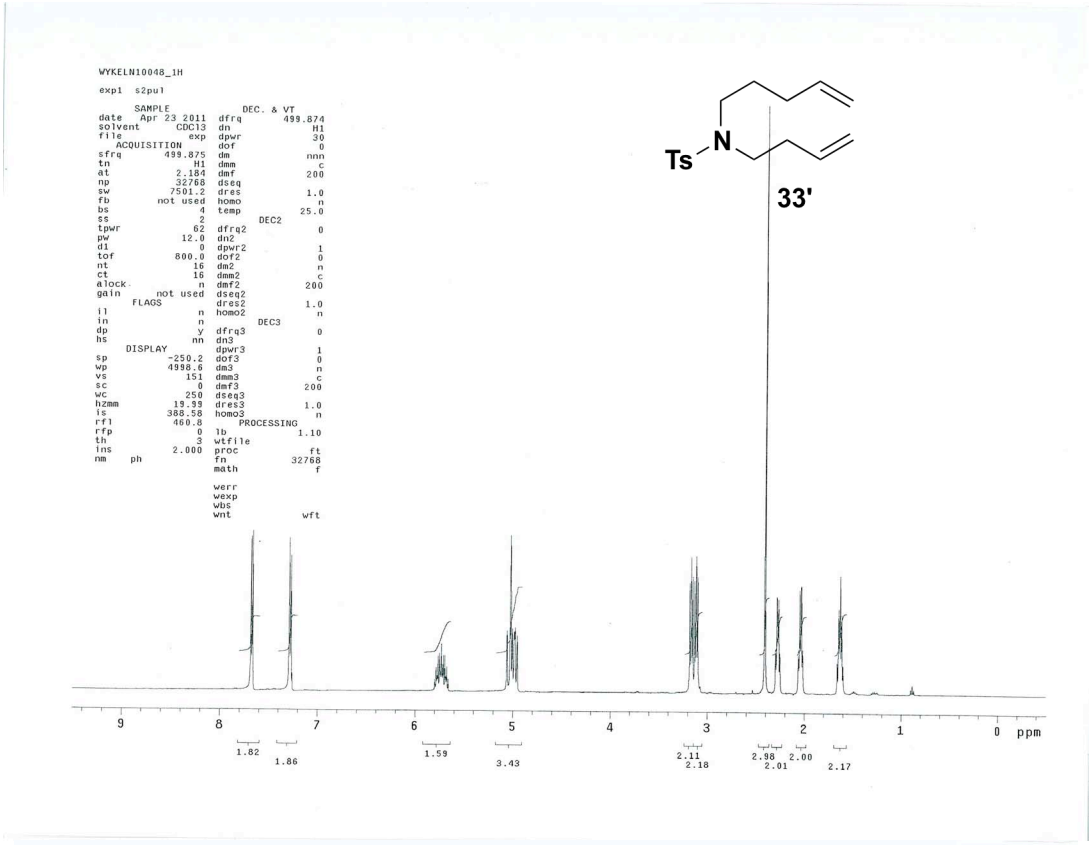

WYKELN11028_13C_benzene
exp1 s2pul
SAMPLE
date Nov 2 2010
solvent Benzene
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN11028~
_13C_benzene.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29986.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 999999
ct 33552
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1044.2
wp 29995.3
vs 1545
sc 0
wc 250
hzmm 3.98
is 500.00
rfl 17133.8
rfp 16088.7
th 5
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 9180
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
PMBO
NMeBoc
Me
N
O
Me
O2N
O
O
45-Z
220
200
180
160
140
120
100
80
60
40
20
ppm

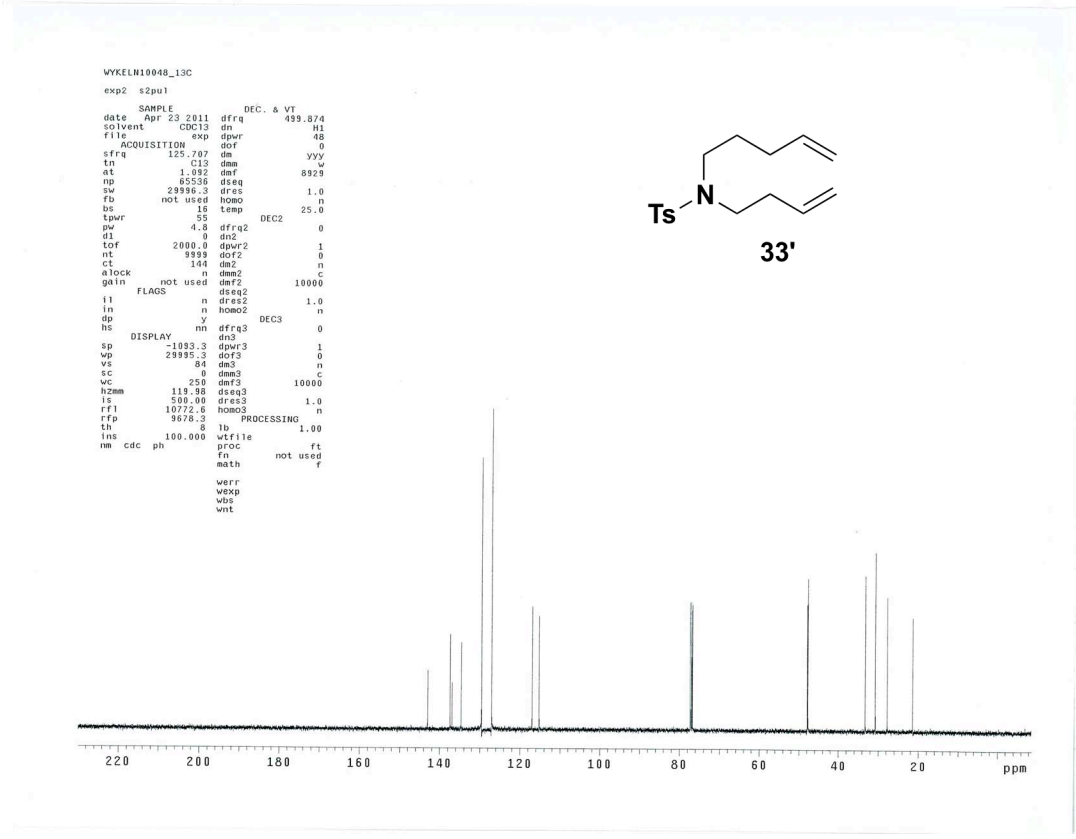

WYKELN11015_1H
exp3 s2pul
SAMPLE
date Oct 26 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 16
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 1024
ct 256
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 126.77
rfl 5130.4
rfp 3631.3
th 1
ins 3.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Me
N
Boc
Me
PMBO
N
O
O2N
Me
O
Si(OEt)2Me
O
32'
9 8 7 6 5 4 3 2 1 0 ppm
1.69
1.46
0.83 3.24
0.56 1.29 0.73
1.45 0.730.52
0.60 4.81 9.38 4.25 1.46
1.92 0.44 2.72 3.95
3.31
2.47 9.22 5.11
2.68 1.21 6.34
3.00

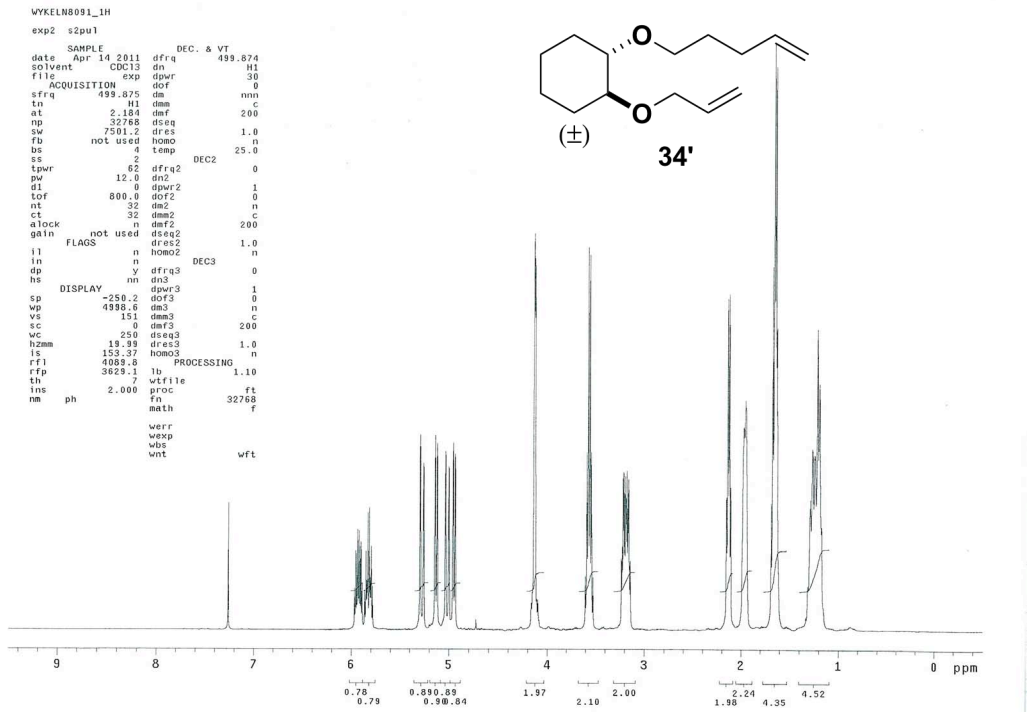

WYKELN11015_13C
exp1 s2pul
SAMPLE
date Oct 26 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Publ/WYKELN11015~
13C.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 999999
ct 36144
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1030.6
wp 29995.3
vs 52
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10269.8
rfp 9678.3
th 88
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 9180
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
wexp
wbs
wnt
Me
N
Boc
Me
PMBO
N
O
O2N
Me
O
Si(OEt)2Me
O
32'
220 200 180 160 140 120 100 80 60 40 20 ppm

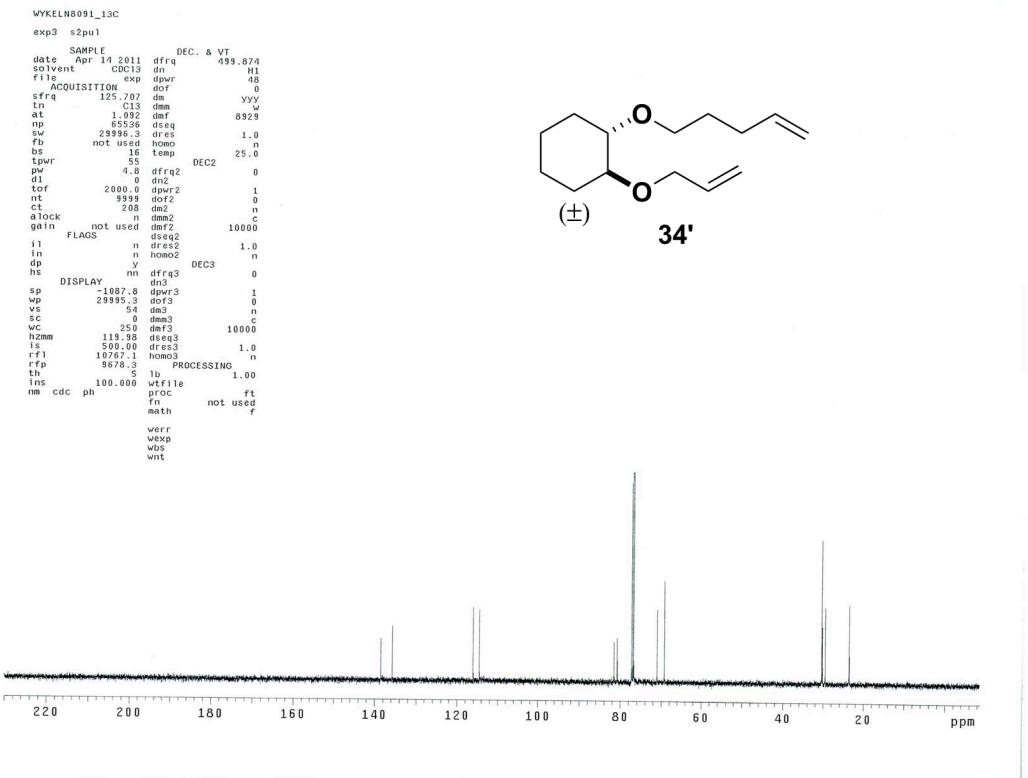

WYKELN11018_1H
exp1 s2pul
SAMPLE
date Oct 27 2010
solvent CDCl3
file /export/home/~ds2/vnmrsys/data/l~500c/schreiber/WAN~G/Pubi/WYKELN11018~_1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 8
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 4998.6
vs 96
sc 0
wc 250
hzmm 19.99
is 347.32
rfl 451.1
rfp 0
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
PMBO
Me
N
Boc
O2N
O
Si(OEt)2Me
32
9 8 7 6 5 4 3 2 1 0 ppm
1.72 0.12 1.23 3.16 0.87 1.00 1.97 12.37 0.99 5.98 4.70 0.93 0.93 0.65 2.06 2.06 9.53 2.03 0.66 2.12 2.06 13.16 0.50 3.04


WYKELN11018_13C
exp1 s2pul
SAMPLE
date Oct 27 2010
solvent CDCl3
file /export/home/~ds2/vnmrsys/data/l~500c/schreiber/WAN~G/Pubi/WYKELN11018~_13C.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 999999
ct 3104
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1095.1
wp 29995.3
vs 104
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10774.4
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 9100
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
PMBO
Me
N
Boc
O2N
O
Si(OEt)2Me
32
220 200 180 160 140 120 100 80 60 40 20 ppm


WYKELN10048_1H
exp1 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 388.58
rfl 460.8
rfp 0
th 3
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
Ts
N
33'
9
8
7
6
5
4
3
2
1
0
ppm
1.82
1.86
1.59
3.43
2.11
2.18
2.98
2.01
2.00
2.17


WYKELN10048_13C
exp2 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 144
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1093.3
wp 29995.3
vs 84
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10772.6
rfp 9678.3
th 8
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Ts
N
33'
220
200
180
160
140
120
100
80
60
40
20
ppm

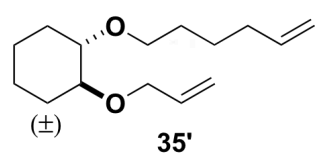

WYKELN8091_1H
exp2 s2pul
SAMPLE
date Apr 14 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 153.37
rfl 4089.8
rfp 3629.1
th 7
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
(±)
34'
9
8
7
6
5
4
3
2
1
0 ppm
0.78
0.79
0.89
0.90
0.89
0.84
1.97
2.10
2.00
2.24
1.98
4.35
4.52


WYKELN8091_13C
exp3 s2pul
SAMPLE
date Apr 14 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 208
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 54
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 5
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
(±)
34'
220
200
180
160
140
120
100
80
60
40
20
ppm

WYKELN8092_1H

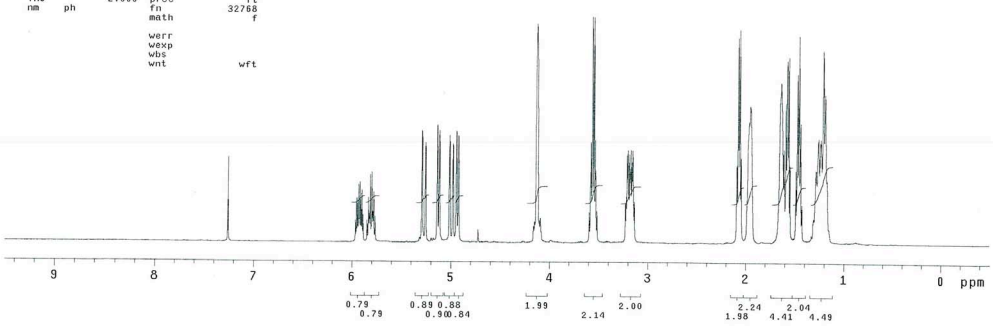
exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 14 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	30
ACQUISITION		dof	0
sfrq	499.875	dm	nnn
tn	H1	dmm	c
at	2.184	dmf	200
np	32768	dseq	
sw	7501.2	dres	1.0
fb	not used	homo	n
bs	4	temp	25.0
ss	2	DEC2	
tpwr	62	dfrq2	0
pw	12.0	dn2	
d1	0	dpwr2	1
tof	800.0	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.2	dof3	0
wp	4998.6	dm3	n
vs	58	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	19.99	dres3	1.0
is	153.37	homo3	n
rfl	4080.3	PROCESSING	
rfp	3629.1	lb	1.10
th	5	wtfile	
ins	2.000	proc	ft
nm ph		fn	32768
		math	f
		werr	
		wexp	
		wbs	
		wnt	wft



(±)

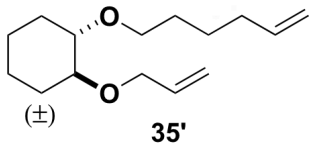
35'



WYKELN8092_13C

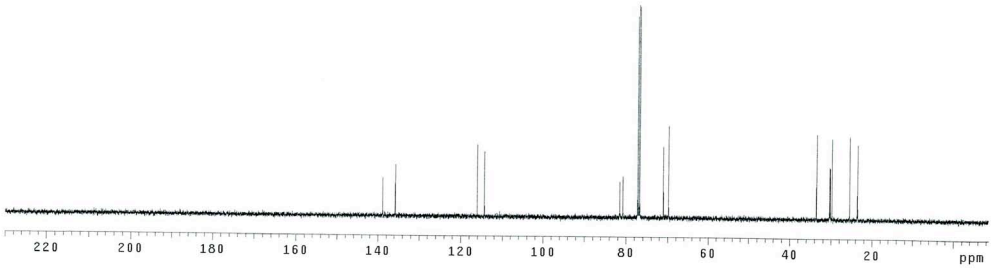
exp3 s2pul

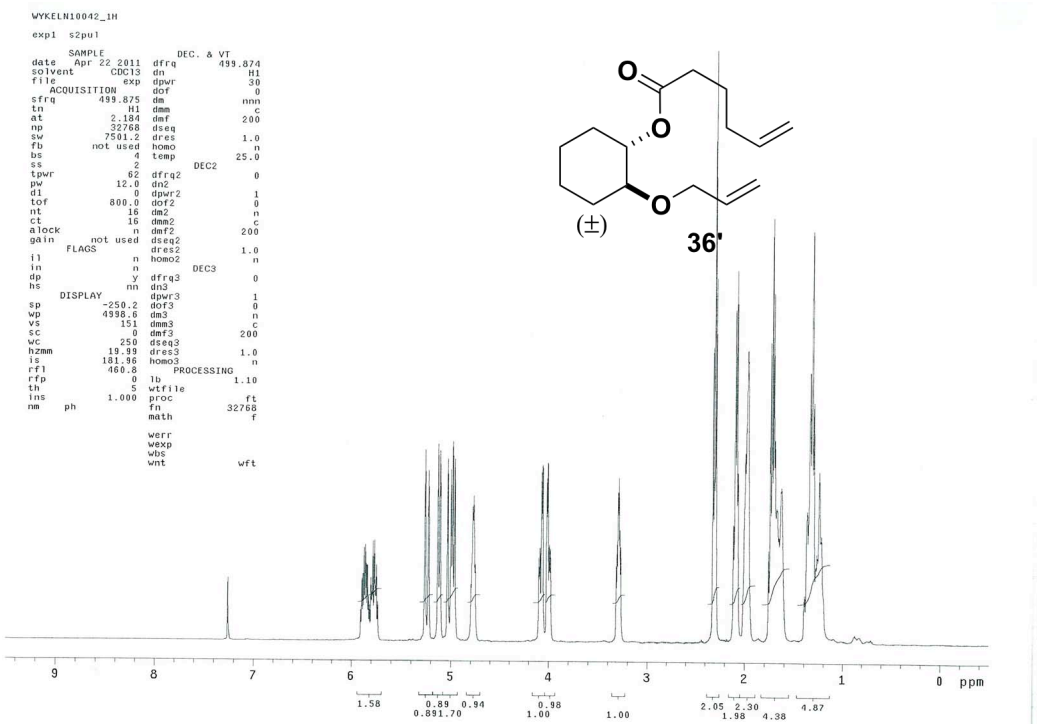
SAMPLE		DEC. & VT	
date	Apr 14 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	8929
np	65536	dseq	
sw	29986.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.8	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	9999	dof2	0
ct	320	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1087.8	dpwr3	1
wp	29995.3	dof3	0
vs	54	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10767.1	homo3	n
rfp	9678.3	PROCESSING	
th	5	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	

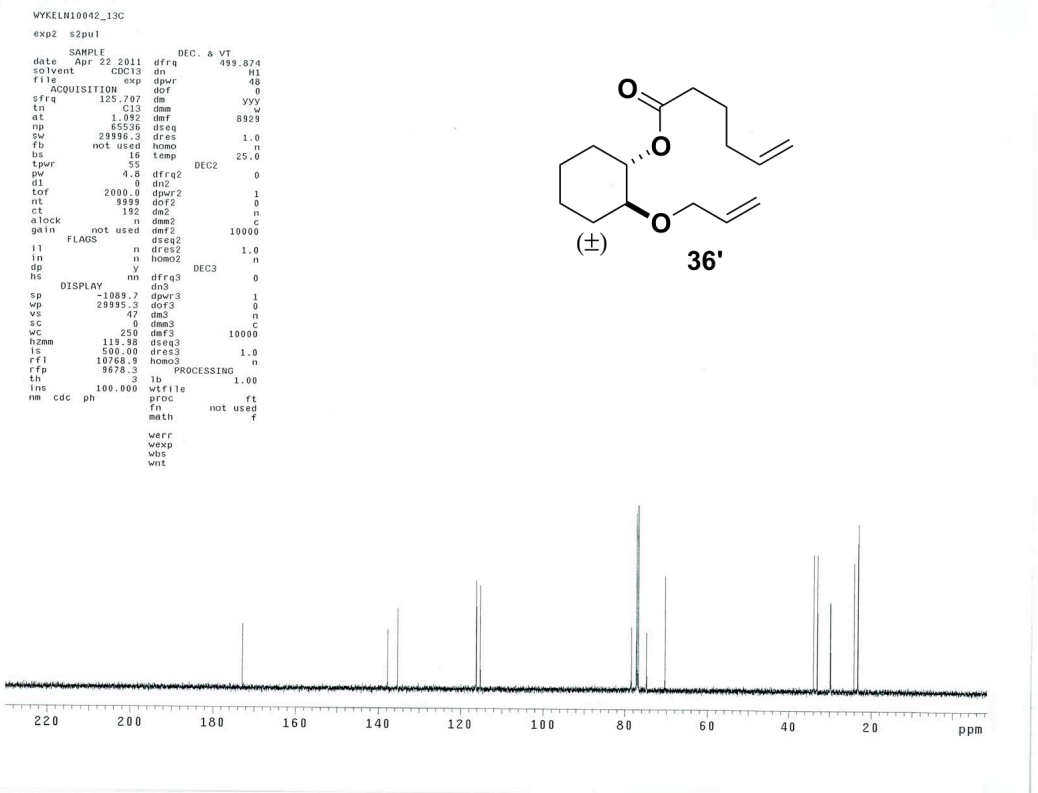


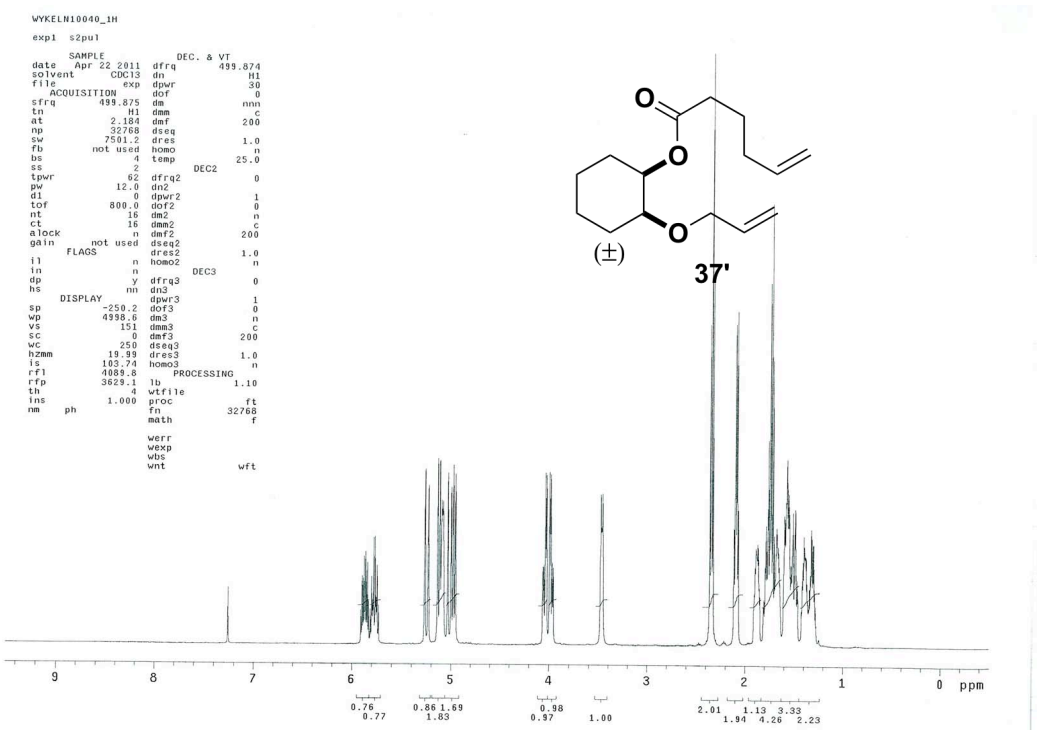
(±)

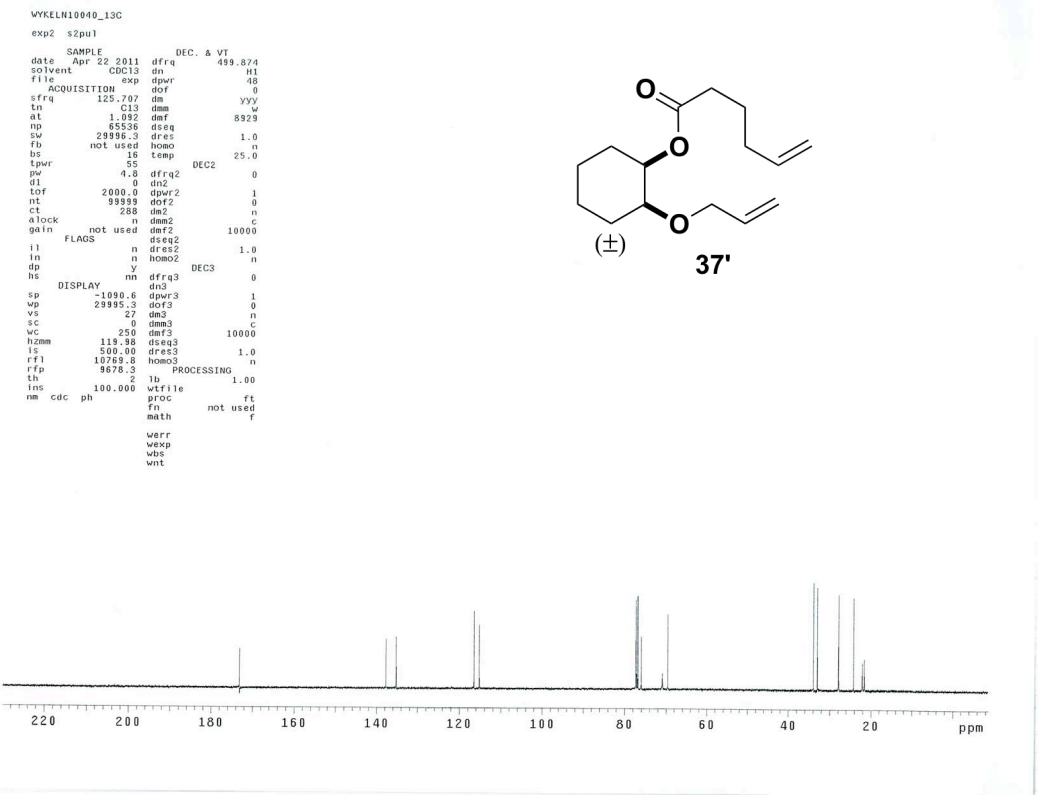
35'

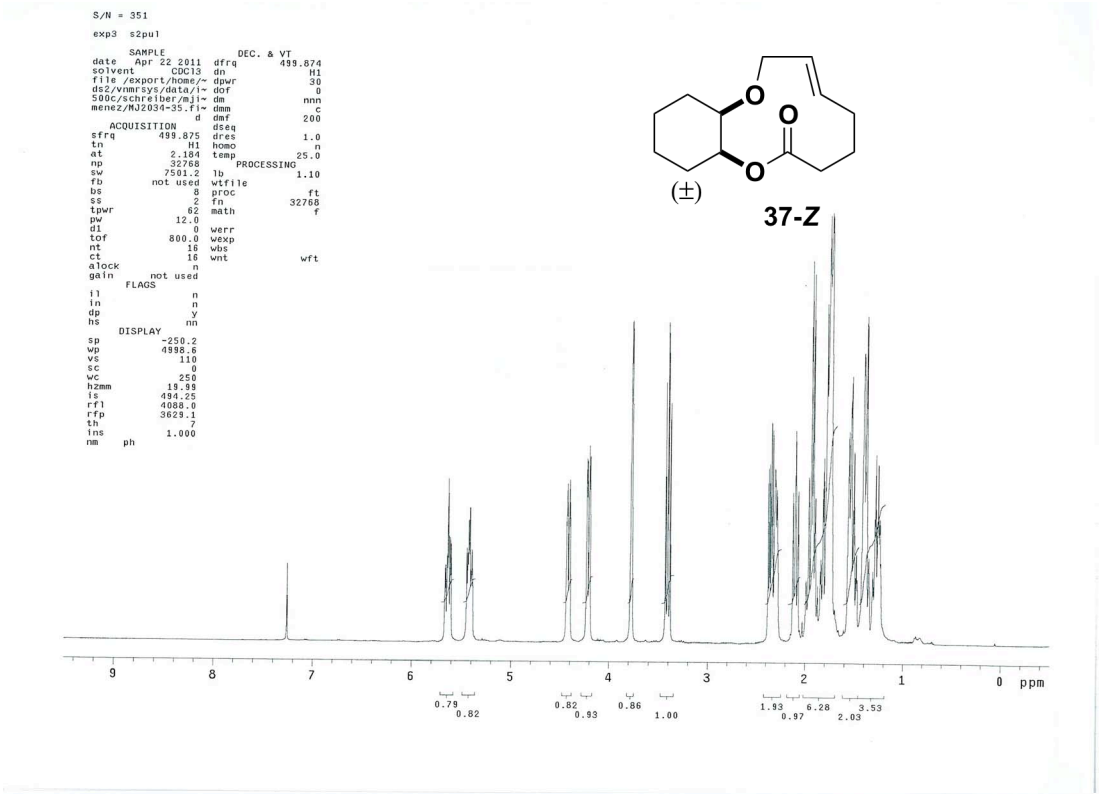


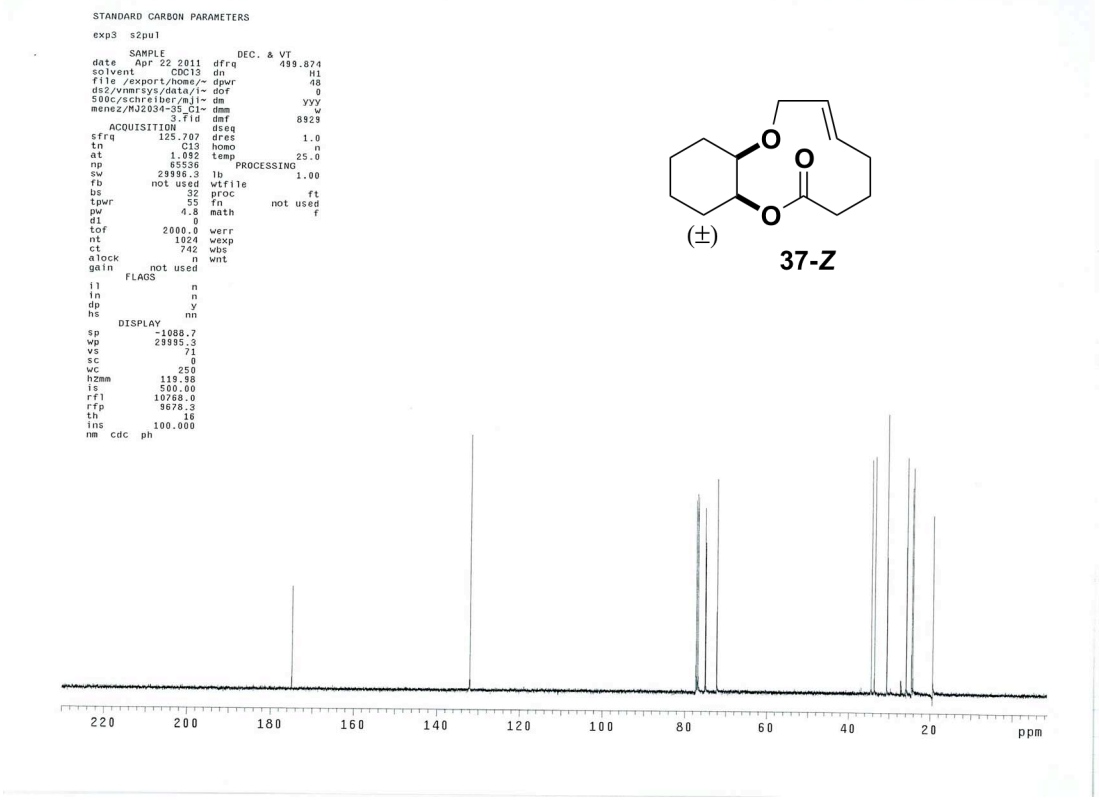

WYKELN10042_1H
exp1 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 181.96
rfl 460.8
rfp 0
th 5
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
(±)
36'
9
8
7
6
5
4
3
2
1
0 ppm
1.58
0.89
0.891.70
0.94
0.98
1.00
1.00
2.05
2.30
1.98
4.38
4.87

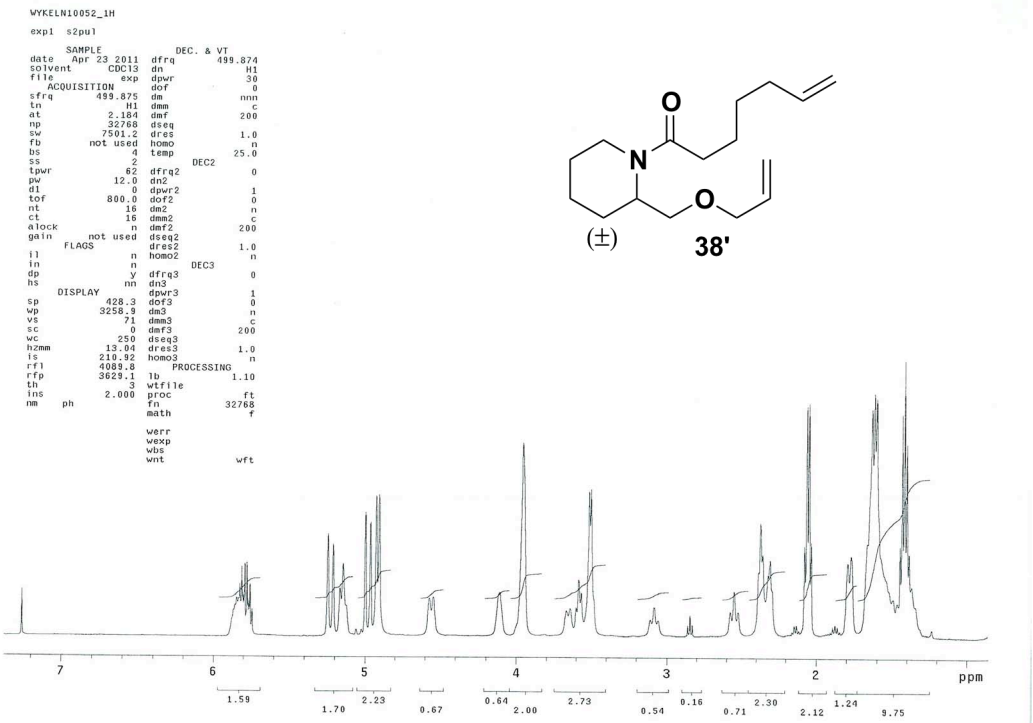

WYKELN10042_13C
exp2 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 192
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1089.7
wp 29995.3
vs 47
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.9
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
36'
220
200
180
160
140
120
100
80
60
40
20
ppm

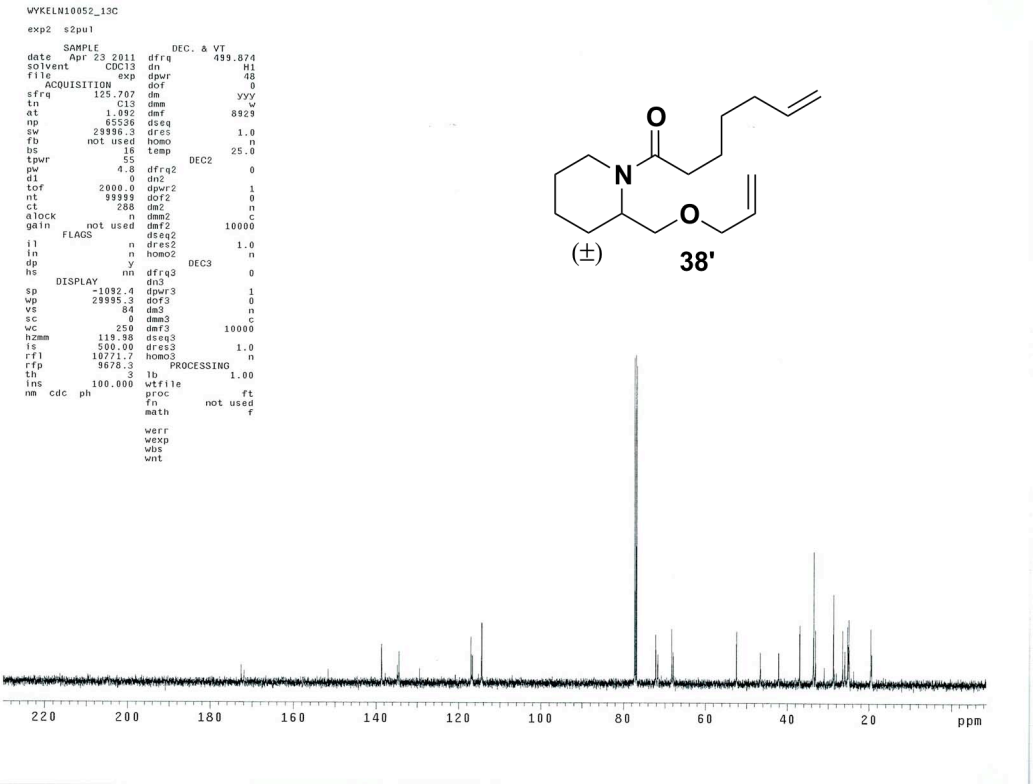

WYKELN10040_1H
exp1 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 103.74
rfl -1089.8
rfp 3629.1
th 4
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
(±)
37'
9
8
7
6
5
4
3
2
1
0 ppm
0.76
0.77
0.86 1.69
1.83
0.98
0.97
1.00
2.01
1.94
1.13 3.33
4.26 2.23

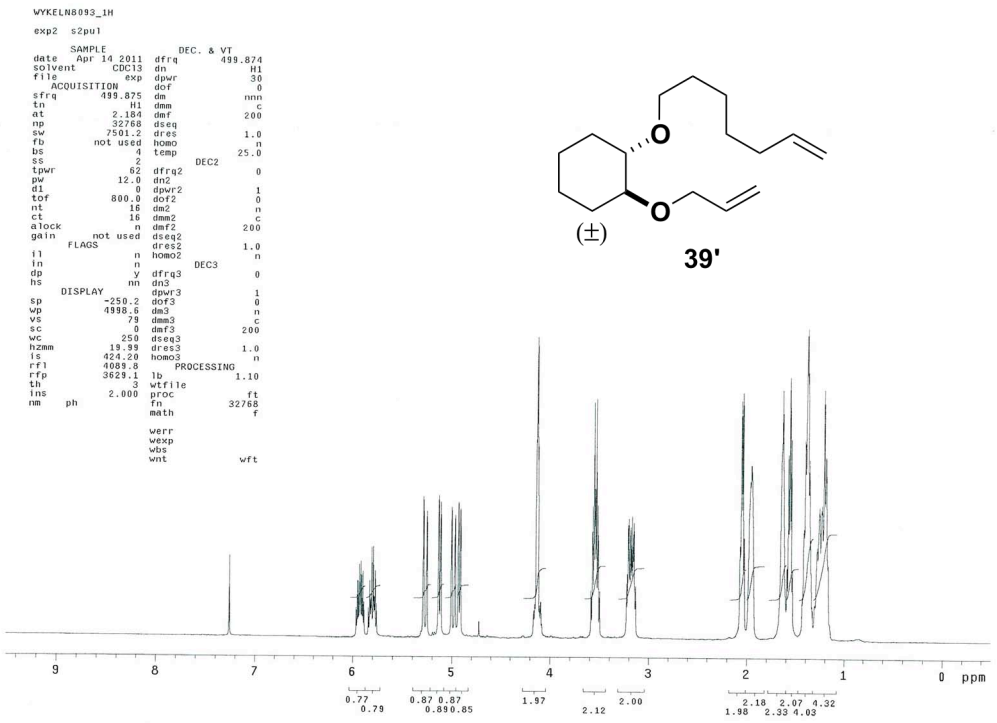

WYKELN10040_13C
exp2 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 99999
ct 288
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1090.6
wp 29995.3
vs 27
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10769.8
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
(±)
37'
220
200
180
160
140
120
100
80
60
40
20
ppm

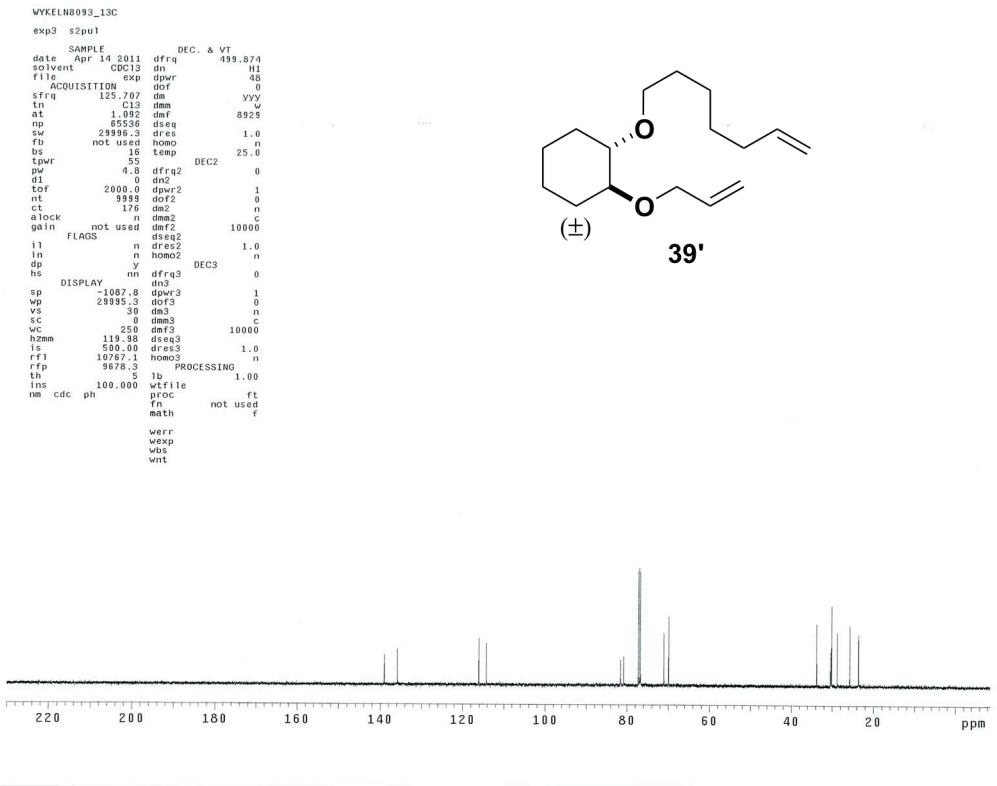

S/N = 351
exp3 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/mji~
menez/MJ2034-35.fi~
d
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 8
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 110
sc 0
wc 250
hzmm 19.98
is 494.25
rfl 4088.0
rfp 3629.1
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
(±)
37-Z
9
8
7
6
5
4
3
2
1
0 ppm
0.79
0.82
0.82
0.93
0.86
1.00
1.93
0.97
6.28
3.53
2.03

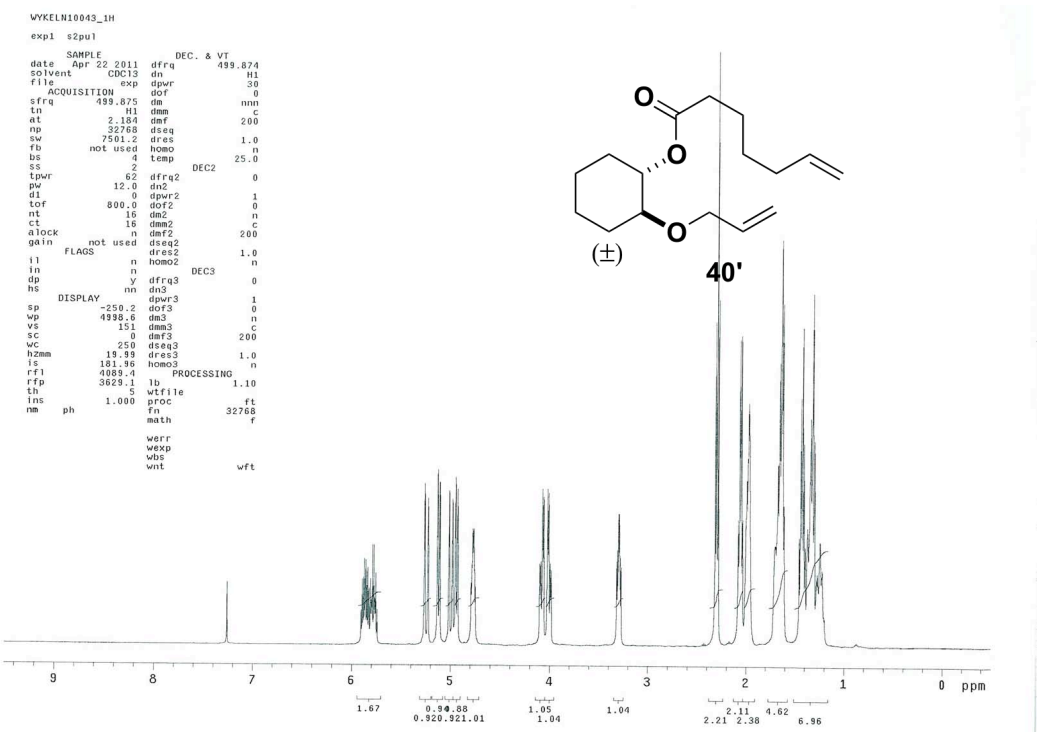

STANDARD CARBON PARAMETERS
exp3 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/mji~
menez/MJ2034-35_C1~
3.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 1024
ct 742
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1088.7
wp 29995.3
vs 71
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.0
rfp 9678.3
th 16
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm W
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
wbs
wnt
(±)
37-Z
220
200
180
160
140
120
100
80
60
40
20
ppm

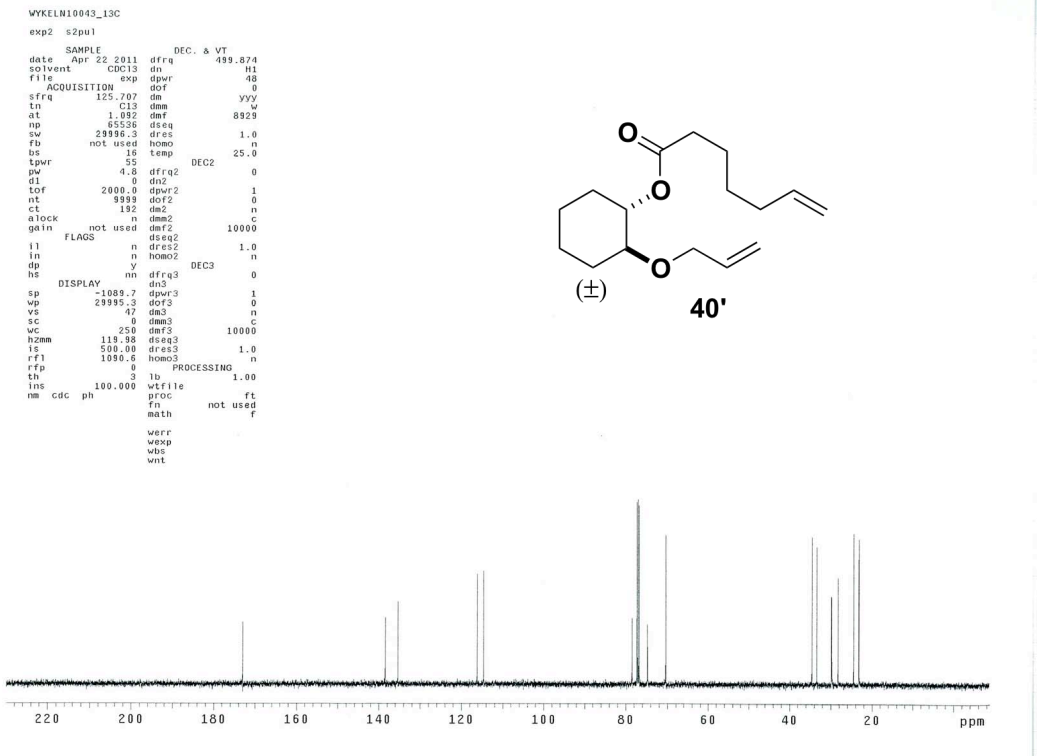

WYKELN10052_1H
exp1 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp 428.3
wp 3258.9
vs 71
sc 0
wc 250
hzmm 13.04
is 210.92
rfl 4089.8
rfp 3629.1
th 3
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
N
O
(±)
38'
7
6
5
4
3
2
ppm
1.59
1.70
2.23
0.67
0.64
2.00
2.73
0.54
0.16
0.71
2.30
2.12
1.24
9.75

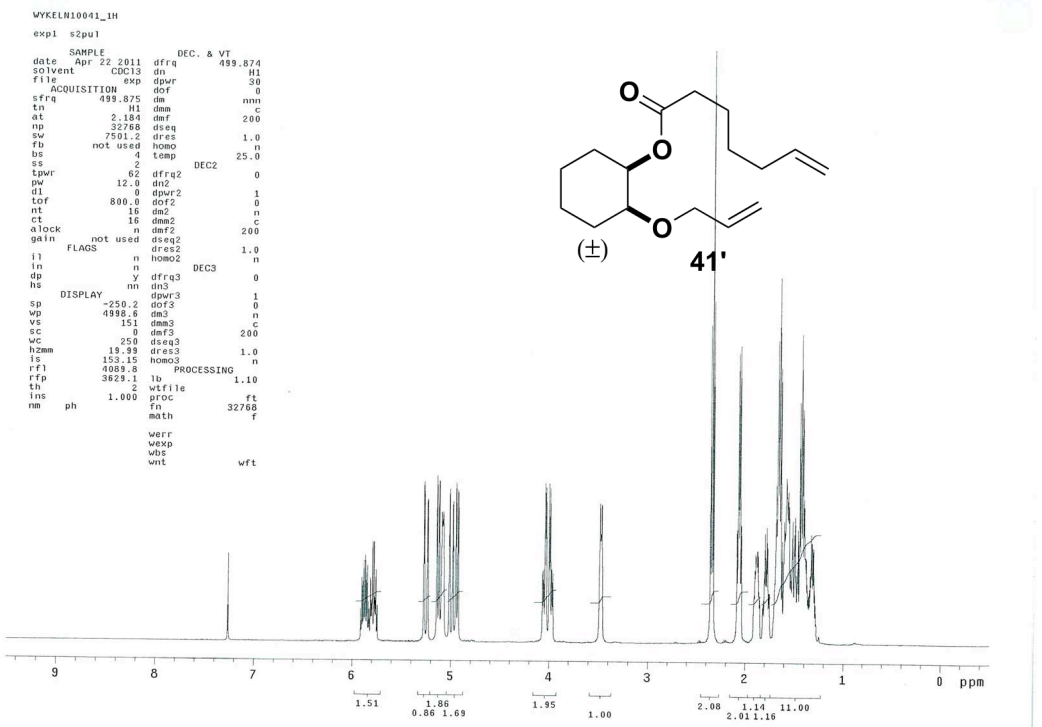

WYKELN10052_13C
exp2 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 99999
ct 288
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1092.4
wp 29995.3
vs 84
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10771.7
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
N
O
(±)
38'
220
200
180
160
140
120
100
80
60
40
20
ppm

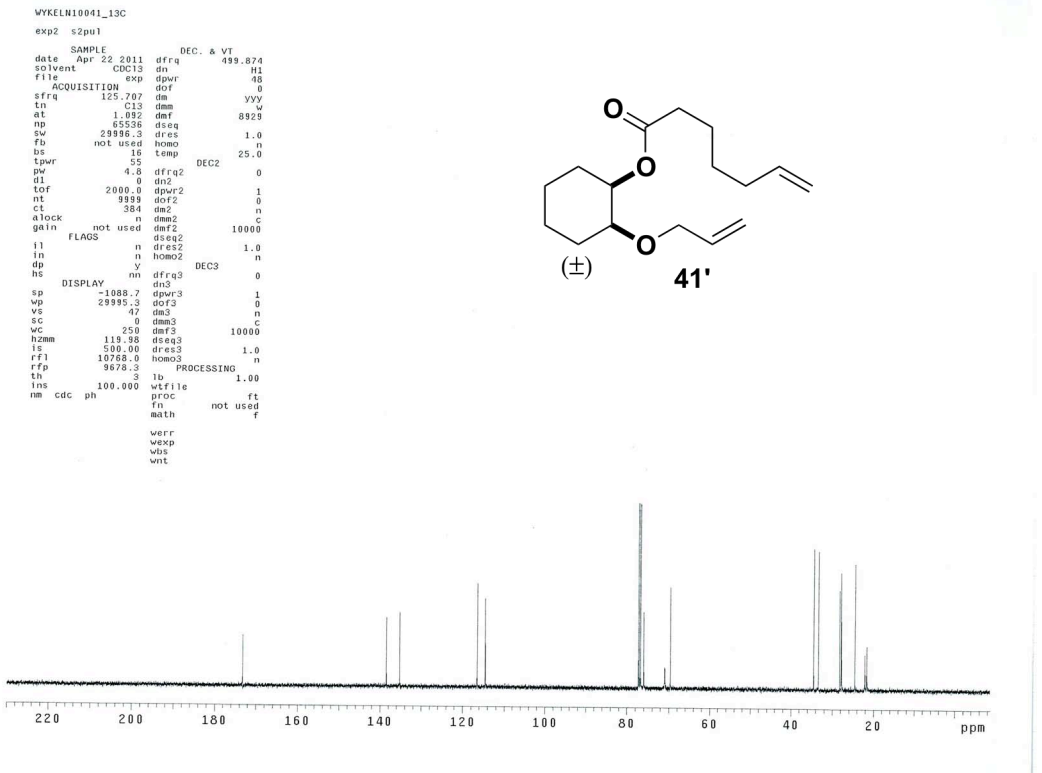

WYKELN8093_1H
exp2 s2pul
SAMPLE
date Apr 14 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 79
sc 0
wc 250
hzmm 19.99
is 424.20
rfl 4089.8
rfp 3629.1
th 3
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
(±)
39'
9
8
7
6
5
4
3
2
1
0 ppm
0.77
0.79
0.87 0.87
0.89 0.85
1.97
2.12
2.00
2.18
1.98
2.07 4.32
2.33 4.03


WYKELN8093_13C
exp3 s2pul
SAMPLE
date Apr 14 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 176
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1087.8
wp 29995.3
vs 30
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10767.1
rfp 9678.3
th 5
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
(±)
39'
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN10043_1H
exp1 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 181.96
rfl 4089.4
rfp 3629.1
th 5
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
(±)
40'
9
8
7
6
5
4
3
2
1
0 ppm
1.67
0.94 0.88
0.92 0.92 1.01
1.05
1.04
1.04
2.11
2.21 2.38
4.62
6.96


WYKELN10043_13C
exp2 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 192
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1089.7
wp 29995.3
vs 47
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 1090.6
rfp 0
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
40'
220
200
180
160
140
120
100
80
60
40
20
ppm

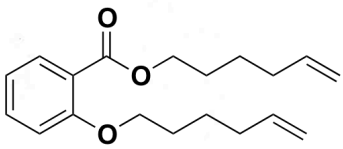

WYKELN10041_1H
expl s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 153.15
rfl 4089.8
rfp 3628.1
th 2
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
O
O
O
(±)
41'
9
8
7
6
5
4
3
2
1
0 ppm
1.51
1.86
0.86 1.69
1.95
1.00
2.08
1.14 11.00
2.01 1.10


WYKELN10041_13C
exp2 s2pul
SAMPLE
date Apr 22 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29986.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 384
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1088.7
wp 29995.3
vs 47
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.0
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
O
O
(±)
41'
220
200
180
160
140
120
100
80
60
40
20
ppm

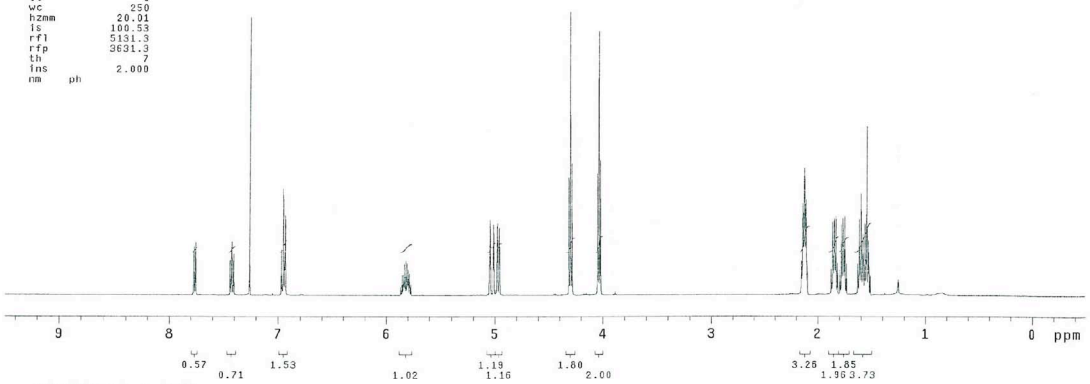
WYKELN5011_byProduct_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Nov 6 2009	dfrq	500.176
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	32
	ds2/vnmrsys/data/i~	dof	0
	500b/schreiber/WAN~	dm	nnn
	G/WYKELN5011_byPro~	dmm	c
	duct_1H.fid	dmf	8770
ACQUISITION		dseq	
sfrq	500.176	dres	1.0
tn	H1	homo	n
at	2.048	temp	23.0
np	32768	PROCESSING	
sw	8000.0	lb	0.10
fb	4000	wtfile	
bs	8	proc	ft
ss	2	fn	not used
tpwr	58	math	f
pw	5.0		
d1	0	werr	
tof	0	wexp	
nt	64	wbs	
ct	64	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5001.5		
vs	65		
sc	0		
wc	250		
hzmm	20.01		
is	100.53		
rfl	5131.3		
rfp	3631.3		
th	7		
ins	2.000		
nm	ph		



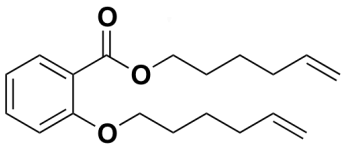
42'



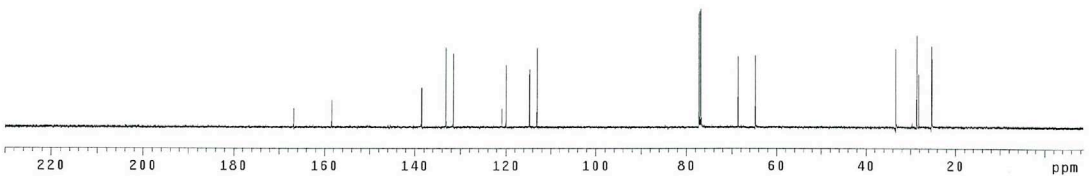
WYKELN5011_byProduct_13C

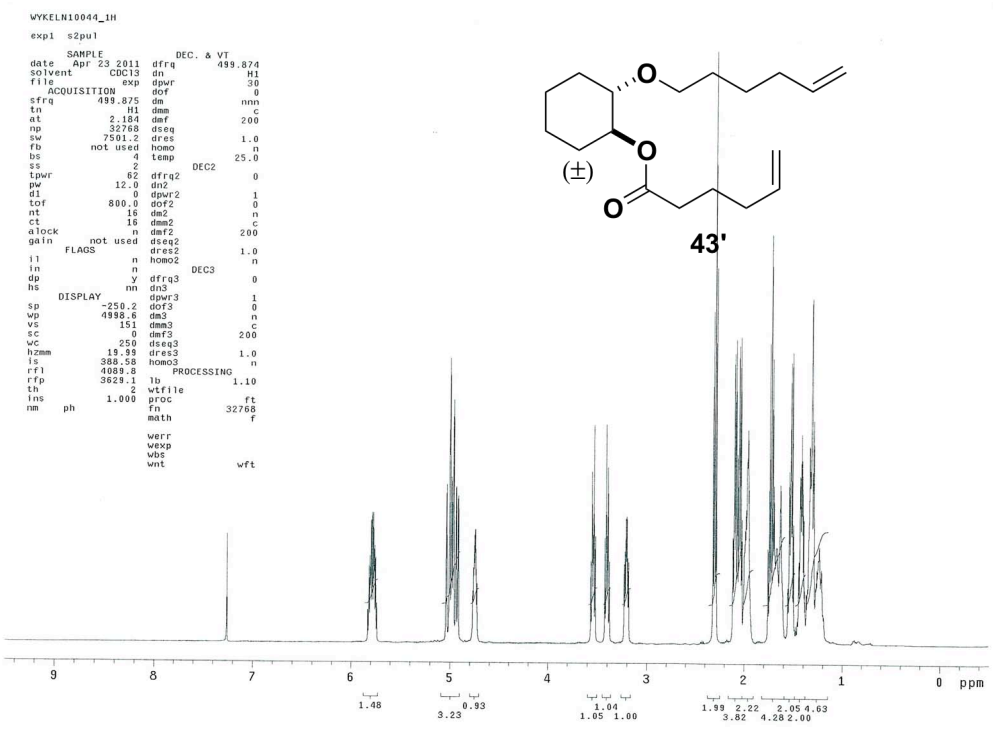
exp2 s2pul

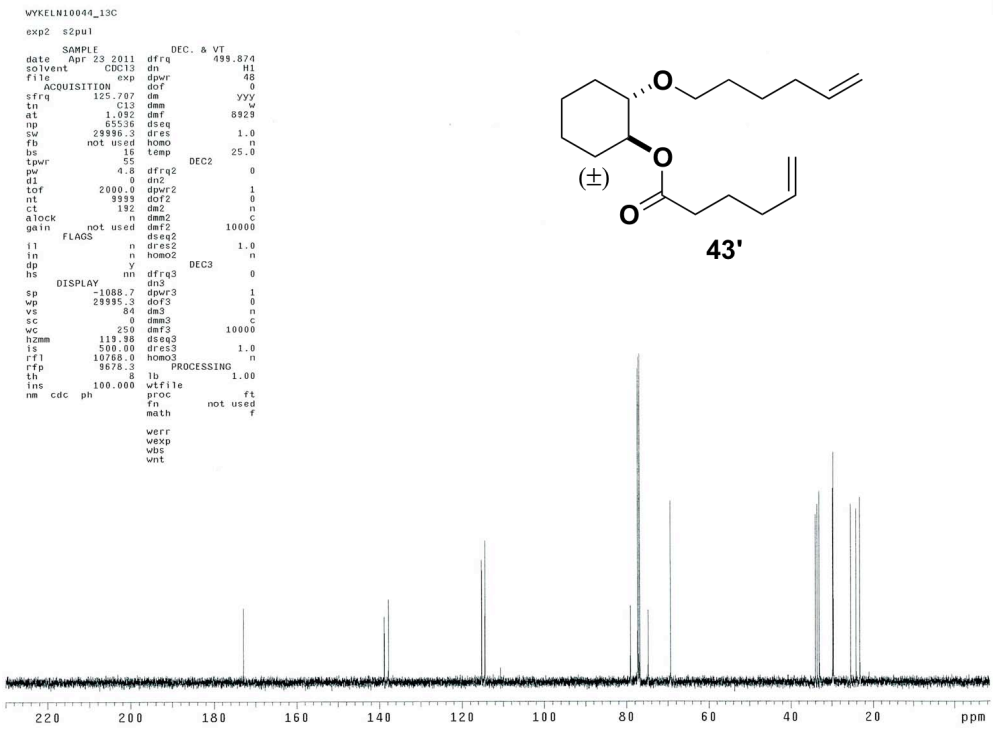
SAMPLE		DEC. & VT	
date	Apr 30 2010	dfrq	499.874
solvent	CDCl3	dn	H1
file	/export/home/~	dpwr	48
	i500c/vnmrsys/data~	dof	0
	/schreiber/WANG/Pu~	dm	yyy
	b1/WYKELN5011_byPr~	dmm	w
	oduct_13C.fid	dmf	10000
ACQUISITION		dseq	
sfrq	125.707	dres	1.0
tn	C13	homo	n
at	1.092	temp	25.0
np	65536	DEC2	
sw	29998.3	dfrq2	0
fb	not used	dn2	
bs	32	dpwr2	1
tpwr	55	dof2	0
pw	4.2	dm2	n
d1	0	dmm2	c
tof	2000.0	dmf2	10000
nt	99999	dseq2	
ct	896	dres2	1.0
alock	n	homo2	n
gain	not used	DEC3	
FLAGS		dfrq3	0
il	n	dn3	
in	n	dpwr3	1
dp	y	dof3	0
hs	nn	dm3	n
DISPLAY		dmm3	c
sp	-1088.7	dmf3	10000
wp	29995.3	dseq3	
vs	27	dres3	1.0
sc	0	homo3	n
wc	250	PROCESSING	
hzmm	5.34	lb	1.00
is	500.00	wtfile	
rfl	10768.0	proc	ft
rfp	9678.3	fn	not used
th	3	math	f
ins	100.000		
nm	cdc ph	werr	
		wexp	
		wbs	
		wnt	

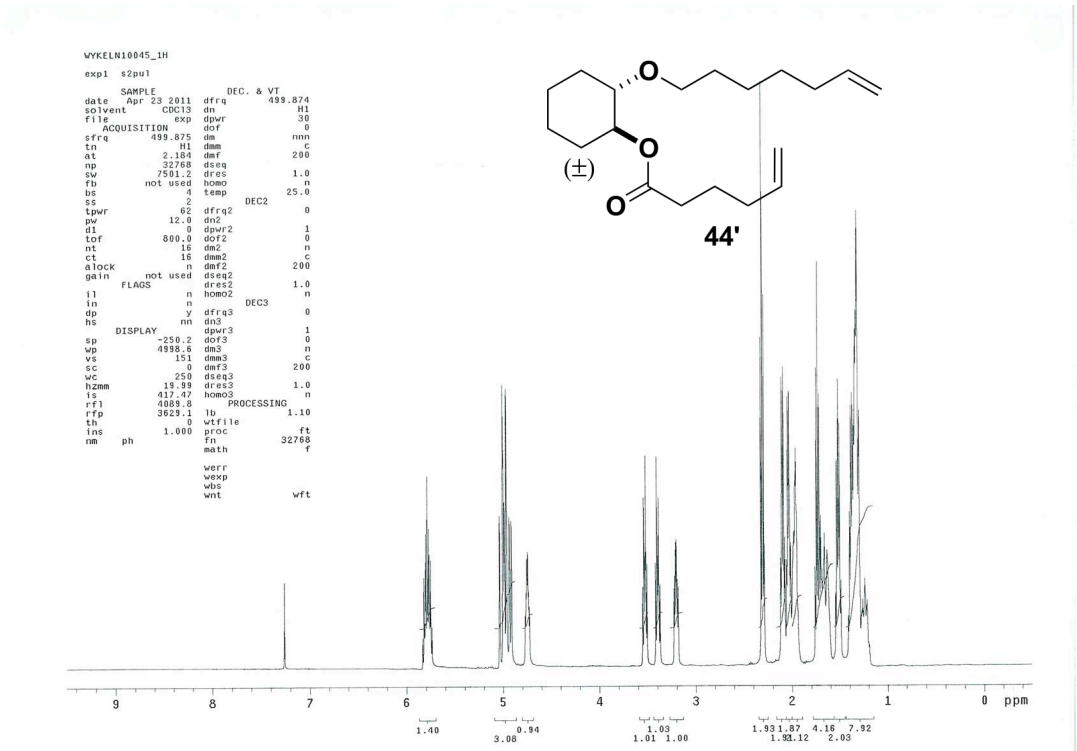


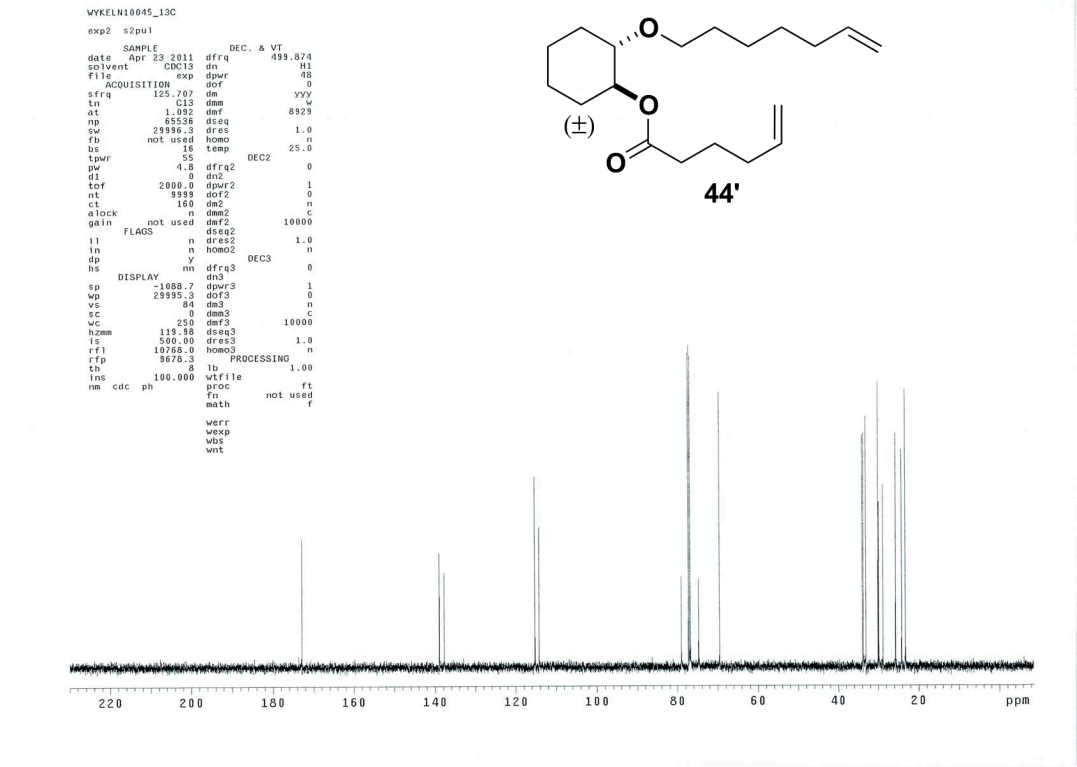
42'

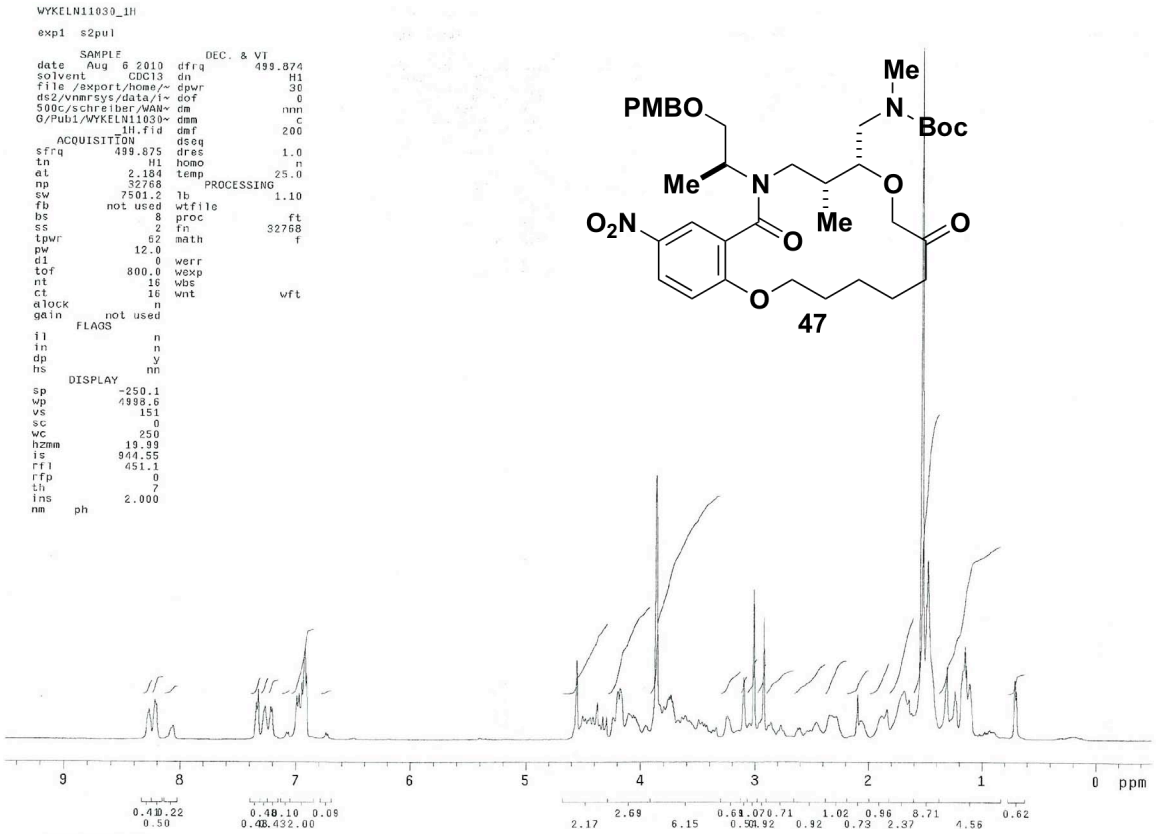


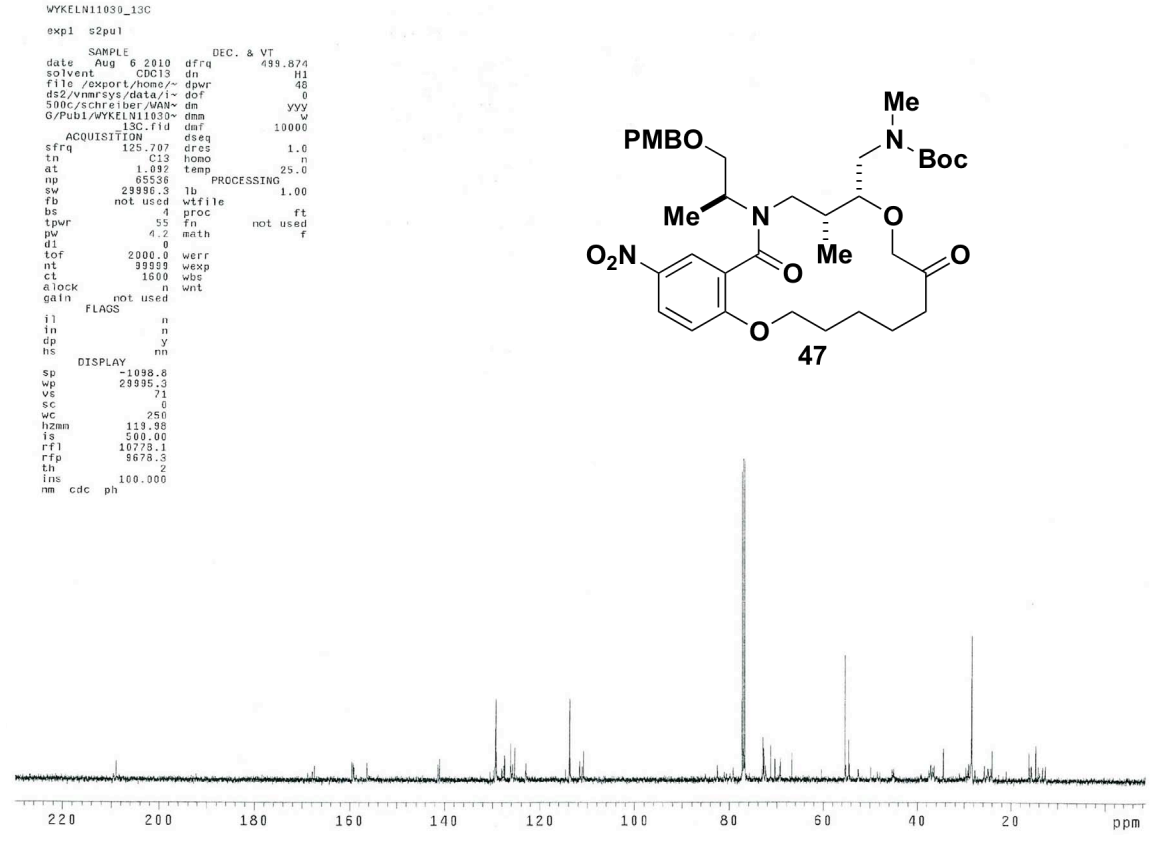

WYKELN10044_1H
exp1 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 388.58
rfl 4089.8
rfp 3629.1
th 2
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
(±)
43'
9
8
7
6
5
4
3
2
1
0 ppm
1.48
0.93
3.23
1.04
1.05 1.00
1.99 2.22 2.05 4.63
3.82 4.28 2.00

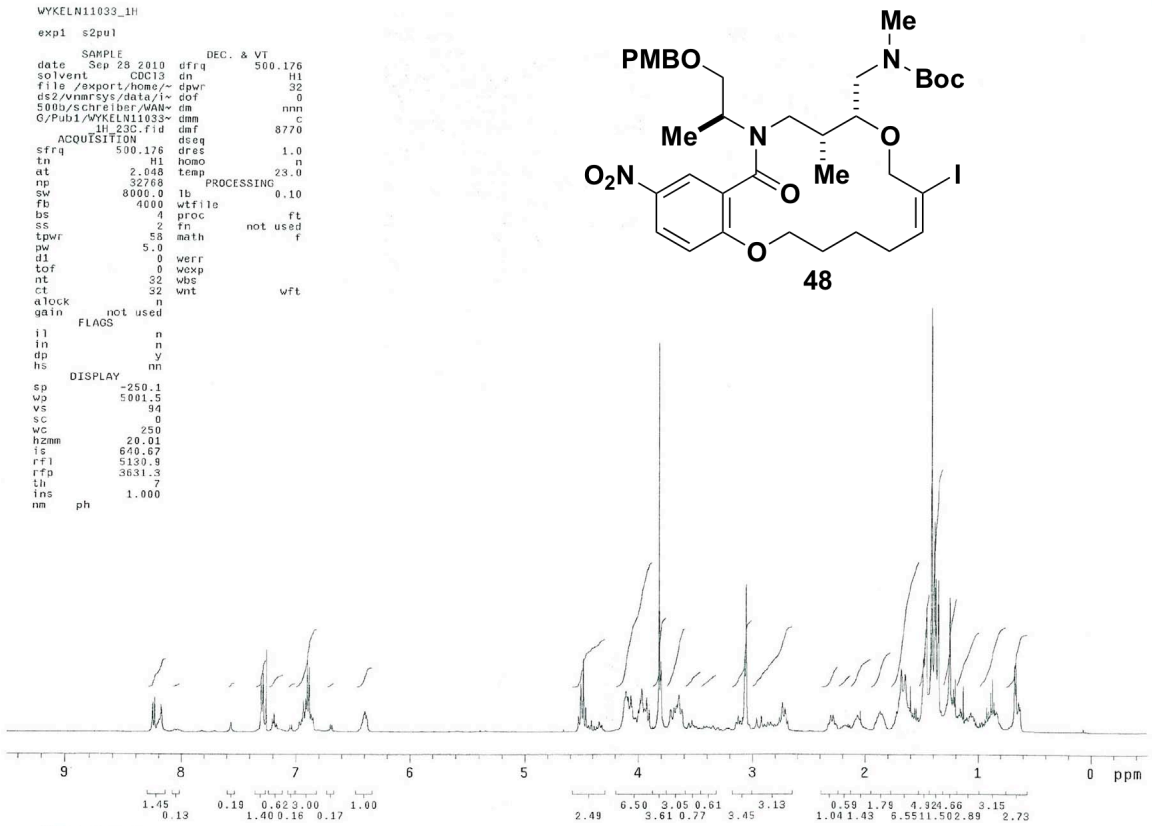

WYKELN10044_13C
exp2 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 192
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1088.7
wp 29995.3
vs 84
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.0
rfp 9678.3
th 8
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
(±)
43'
220
200
180
160
140
120
100
80
60
40
20
ppm

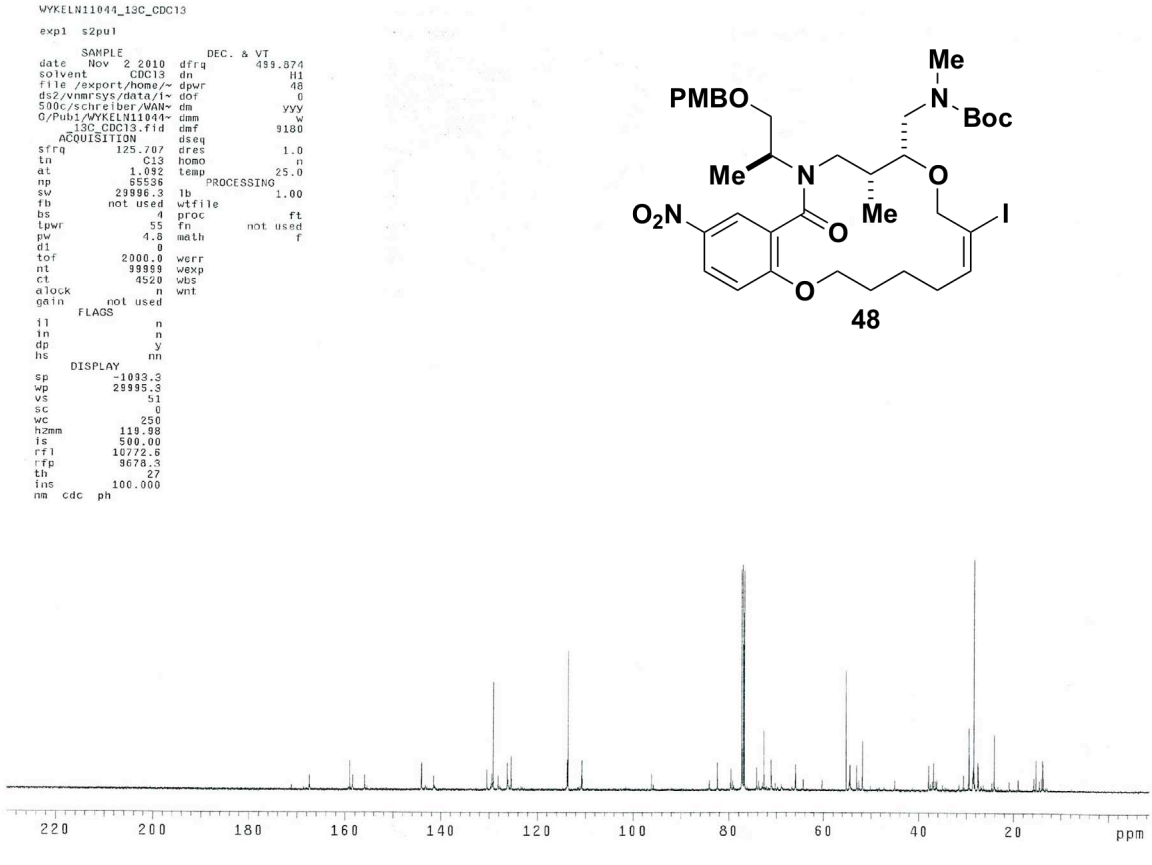

WYKELN10045_1H
exp1 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
dl 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 417.47
rfl 4089.8
rfp 3629.1
th 0
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
(±)
44'
9 8 7 6 5 4 3 2 1 0 ppm
1.40
0.94
3.08
1.03
1.01 1.00
1.93 1.87 4.16 7.92
1.94 4.12 2.03

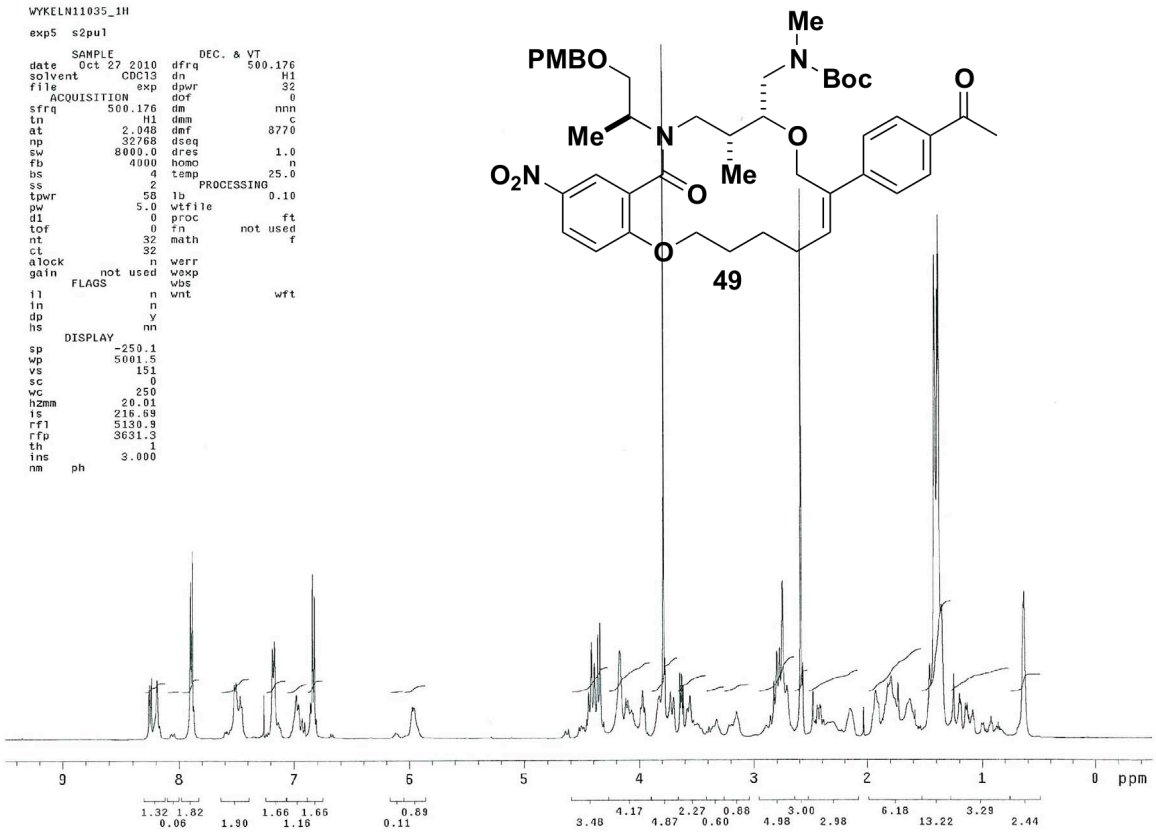

WYKELN10045_13C
exp2 s2pul
SAMPLE
date Apr 23 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
dl 0
tof 2000.0
nt 9999
ct 160
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1088.7
wp 29995.3
vs 84
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10768.0
rfp 9678.3
th 8
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
(±)
44'
220 200 180 160 140 120 100 80 60 40 20 ppm

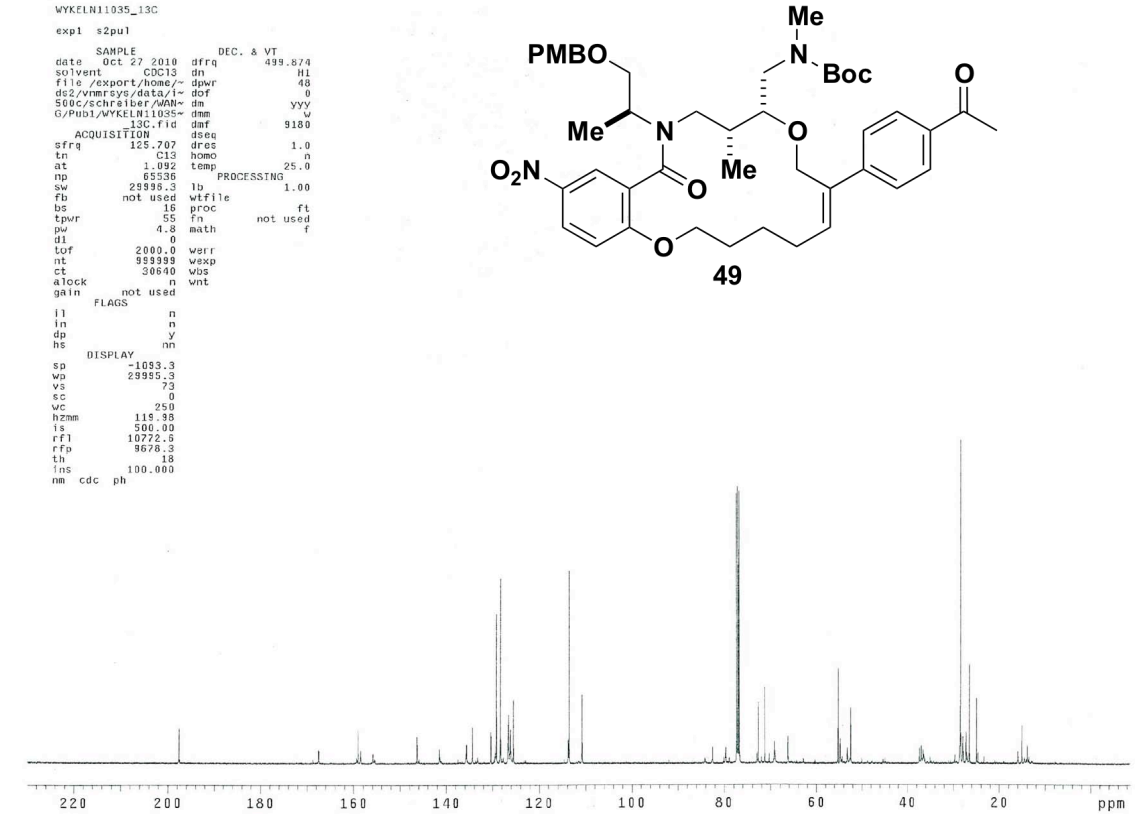

WYKELN11030_1H
exp1 s2pul
SAMPLE
date Aug 6 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN11030~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 8
ss 2
tpwr 52
pw 12.0
d1 0
tof 800.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 944.55
rfl 451.1
rfp 0
th 7
ins 2.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
PMBO
Me
N
Boc
Me
N
O
Me
O
O2N
O
O
O
47
9
8
7
6
5
4
3
2
1
0 ppm
0.41 0.22
0.50
0.48 0.10 0.09
0.48 3.00
2.17
2.69
6.15
0.61 1.07 0.71
0.50 1.92
1.02 0.96 8.71
0.92 0.73 2.37
0.62
4.56

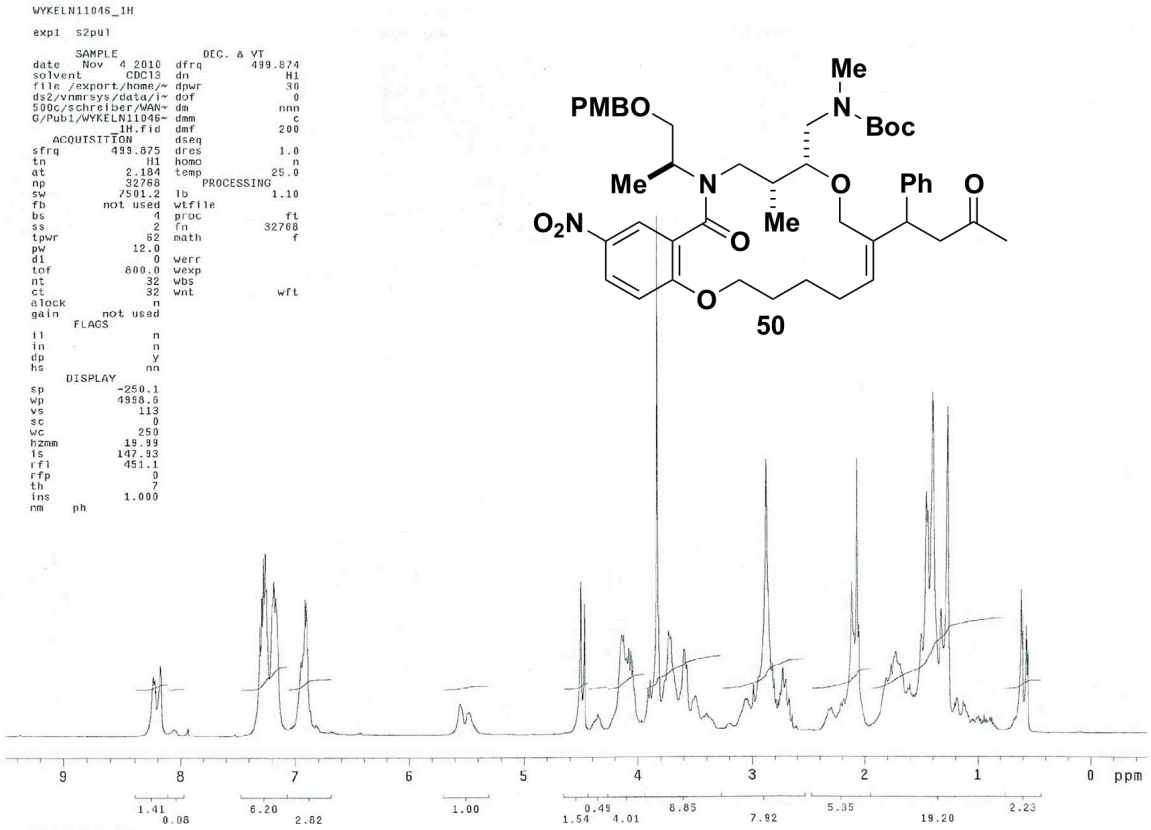

WYKELN11030_13C
exp1 s2pul
SAMPLE
date Aug 6 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN11030~
13C.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 4
tpwr 55
pw 4.2
d1 0
tof 2000.0
nt 99999
ct 1600
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1098.8
wp 29995.3
vs 71
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10773.1
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 10000
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
PMBO
Me
N
Boc
Me
N
O
Me
O
O2N
O
O
O
47
220
200
180
150
140
120
100
80
60
40
20
ppm

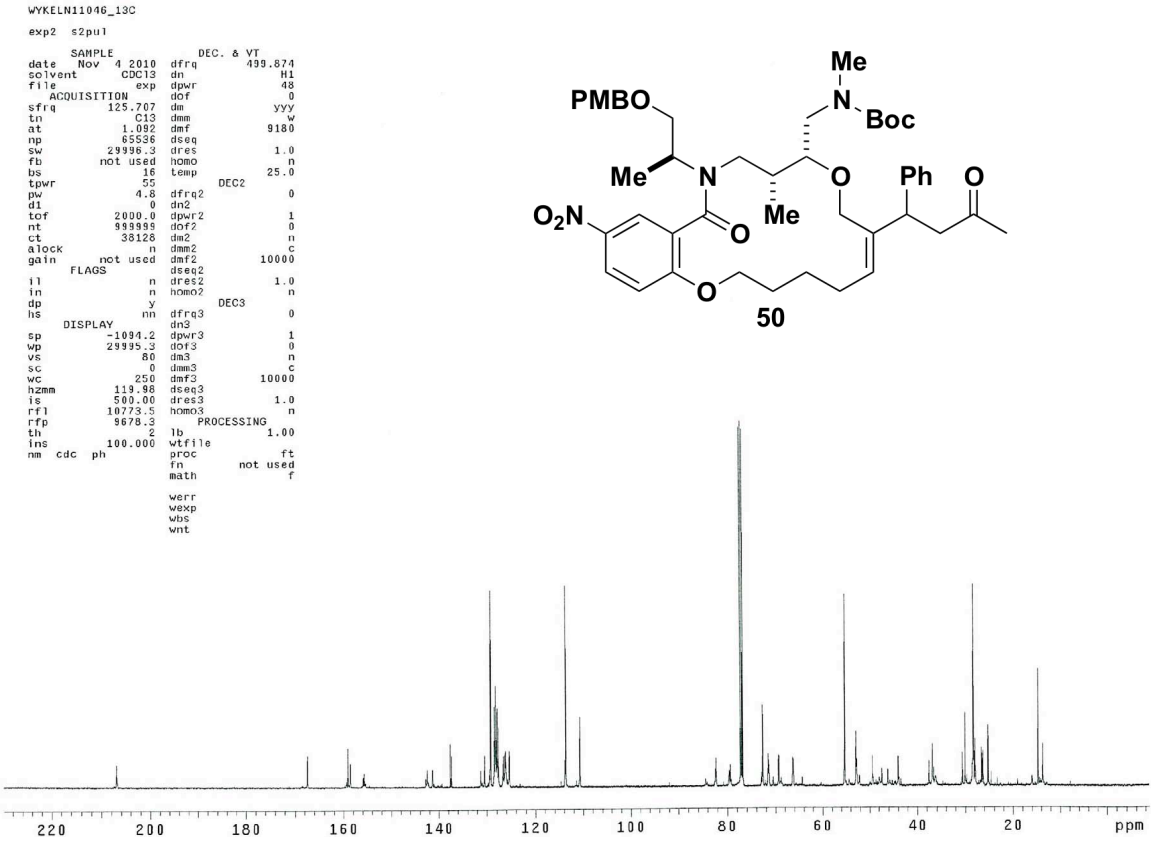

WYKELN11033_1H
exp1 s2pul
SAMPLE
date Sep 28 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500b/schreiber/WAN~
G/Pub1/WYKELN11033~
1H_23C.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 94
sc 0
wc 250
hzmm 20.01
is 640.67
rfl 5130.9
rfp 3631.3
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
PMBO
Me
N
Boc
Me
N
O
O2N
O
Me
I
O
48
9
8
7
6
5
4
3
2
1
0 ppm
1.45
0.13
0.19
0.62
1.40
3.00
0.16
0.17
1.00
2.49
6.50
3.61
3.05
0.77
0.61
3.45
3.13
0.59
1.04
1.79
1.43
4.92
5.55
4.66
11.50
3.15
2.89
2.73

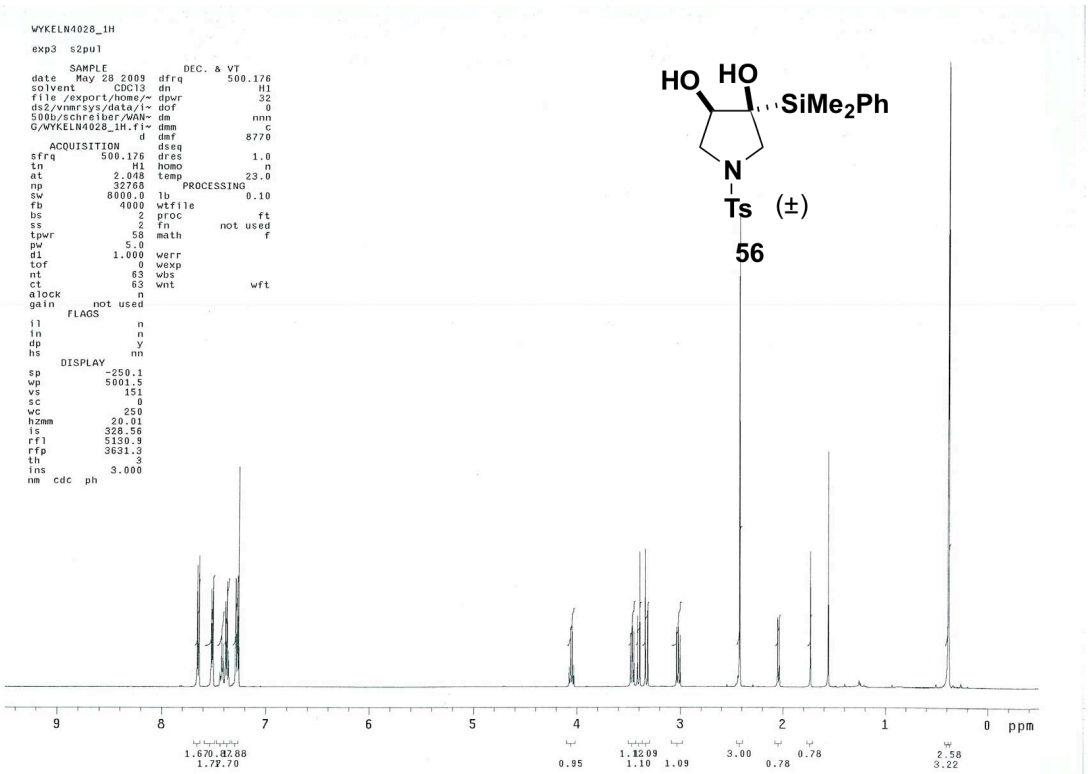

WYKELN11044_13C_CDCl3
exp1 s2pul
SAMPLE
date Nov 2 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN11044~
13C_CDCl3.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 4
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 99999
ct 4520
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1033.3
wp 29995.3
vs 51
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10772.6
rfp 9678.3
th 27
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 9180
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
PMBO
Me
N
Boc
Me
N
O
O2N
O
Me
I
O
48
220
200
180
160
140
120
100
80
60
40
20
ppm

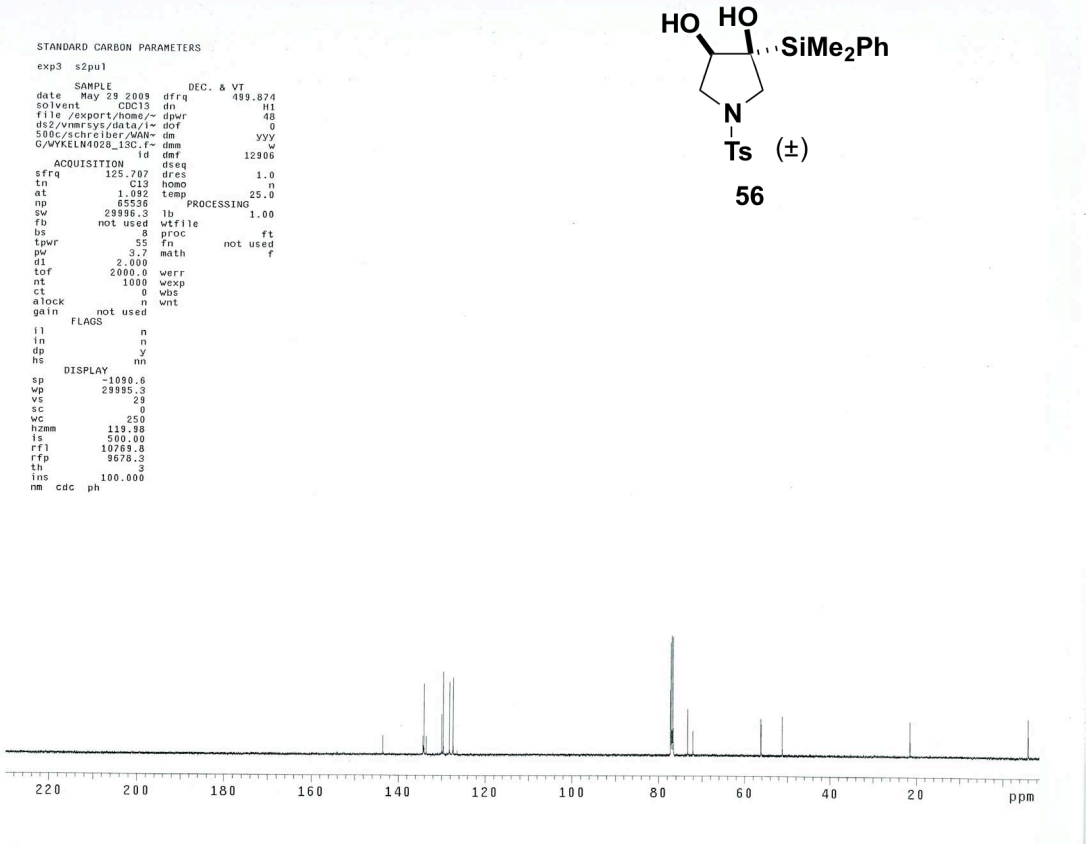

WYKELN11035_1H
exp5 s2pul
SAMPLE
date Oct 27 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 216.69
rfl 5130.9
rfp 3631.3
th 1
ins 3.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Me
N
Boc
O
PMBO
Me
N
O
Me
O2N
O
O
49
9
8
7
6
5
4
3
2
1
0 ppm
1.32 1.82
0.06
1.90
1.66 1.65
1.16
0.89
0.11
4.17
3.48
2.27 0.88
4.87 0.60
3.00
4.98 2.98
6.18
13.22
3.29
2.44

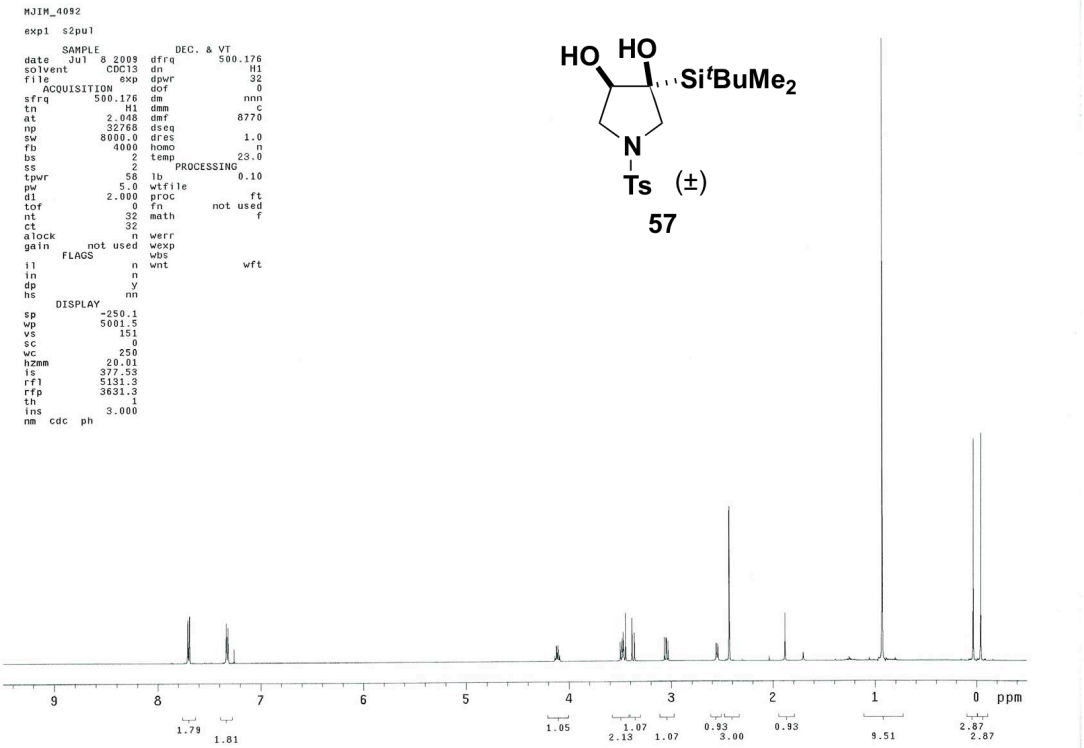

WYKELN11035_13C
exp1 s2pul
SAMPLE
date Oct 27 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/PUb1/WYKELN11035~
_13C.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29998.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 999999
ct 30640
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1093.3
wp 29995.3
vs 73
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10772.6
rfp 9678.3
th 18
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 9180
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Me
N
Boc
O
PMBO
Me
N
O
Me
O2N
O
O
49
220
200
180
160
140
120
100
80
60
40
20
ppm

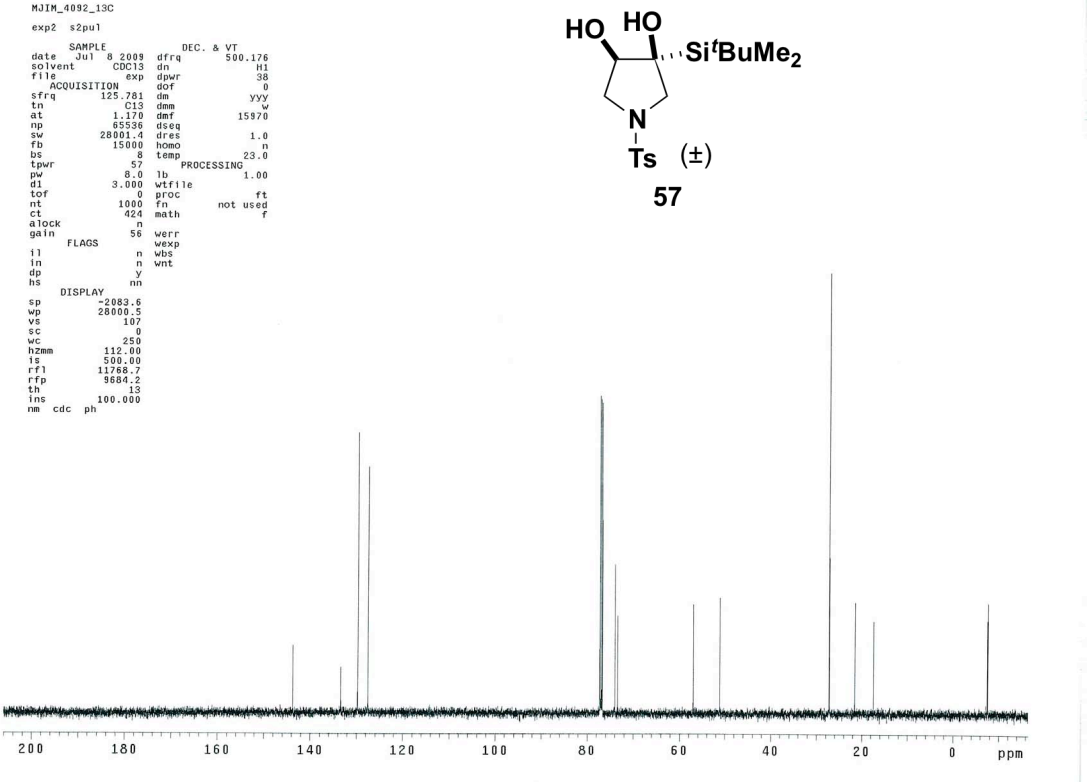

WYKELN11046_1H
exp1 s2pul
SAMPLE
date Nov 4 2010
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/WAN~
G/Pub1/WYKELN11046~
1H.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 4998.6
vs 113
sc 0
wc 250
hzmm 19.99
is 147.93
rfl 451.1
rfp 0
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
PMBO
Me
N
Boc
Me
N
O
Ph
O
O2N
O
Me
O
50
9
8
7
6
5
4
3
2
1
0 ppm
1.41
0.08
6.20
2.62
1.00
0.49
1.54
4.01
8.85
7.92
5.35
19.20
2.23

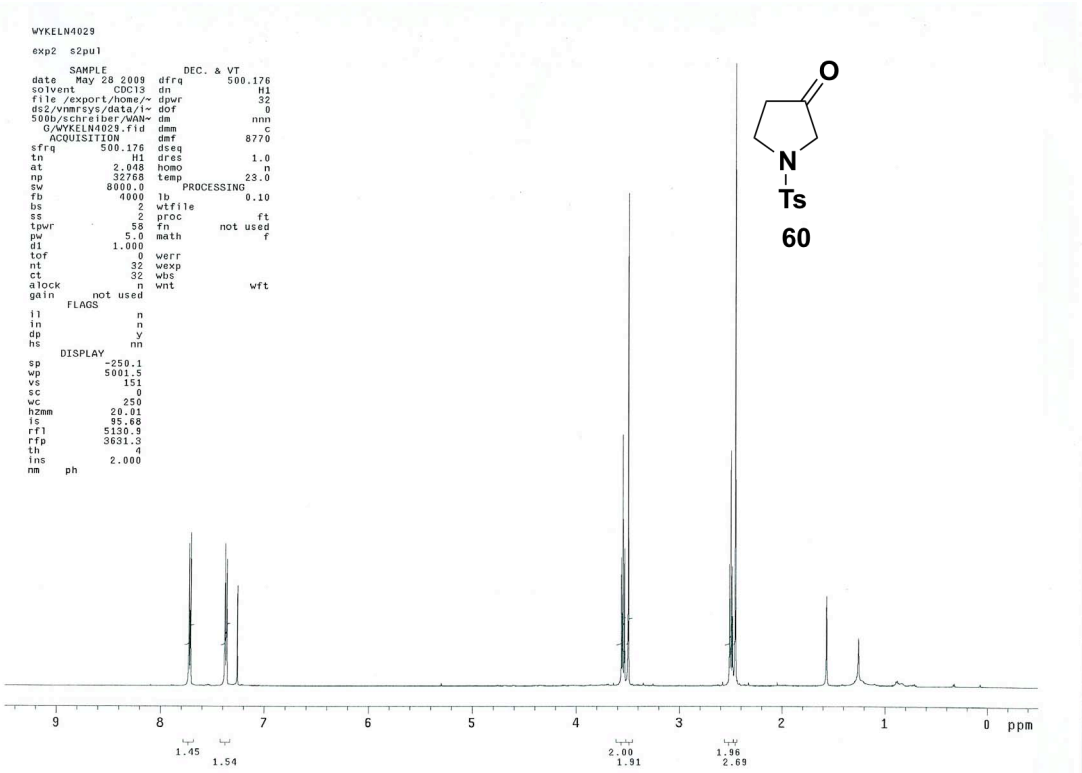

WYKELN11046_13C
exp2 s2pul
SAMPLE
date Nov 4 2010
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 999999
ct 38128
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1094.2
wp 29995.3
vs 80
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10773.5
rfp 9678.3
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 9180
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
PMBO
Me
N
Boc
Me
N
O
Ph
O
O2N
O
Me
O
50
220
200
180
160
140
120
100
80
60
40
20
ppm

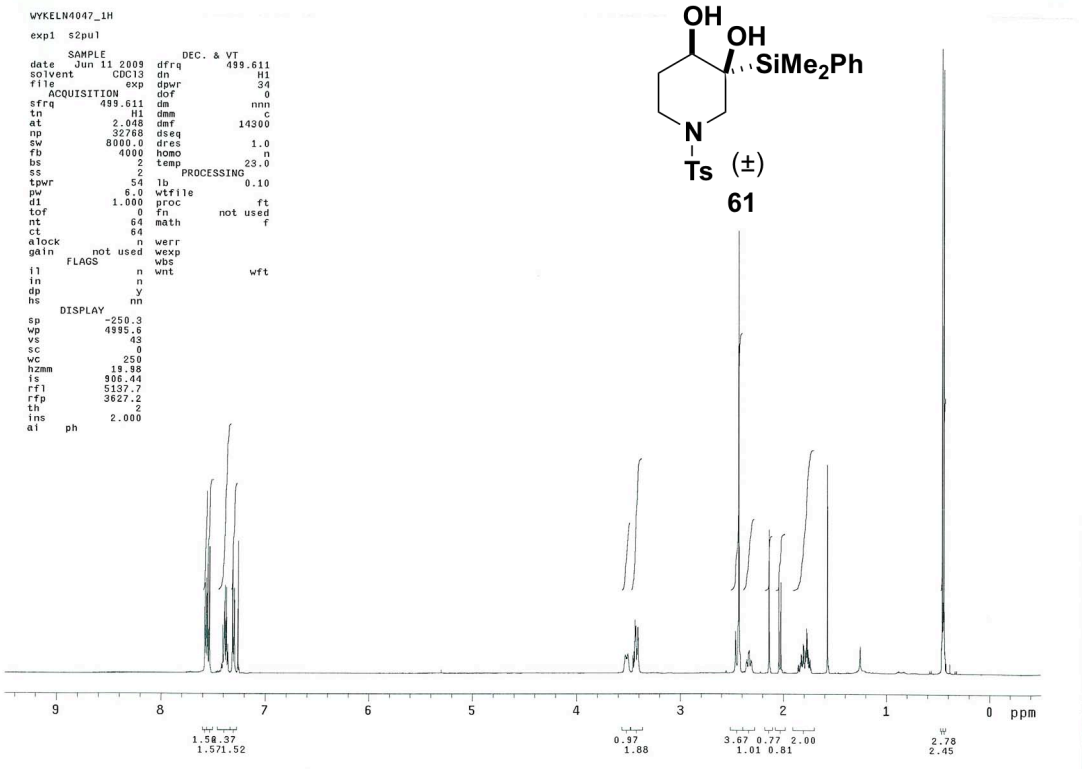

WYKELN4028_1H
exp3 s2pul
SAMPLE
date May 28 2009
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500b/schreiber/WAN~
G/WYKELN4028_1H.fi~
d
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 58
pw 5.0
d1 1.000
tof 0
nt 63
ct 63
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 328.56
rfl 5130.9
rfp 3631.3
th 3
ins 3.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
HO
HO
SiMe2Ph
N
Ts (±)
56
9
8
7
6
5
4
3
2
1
0 ppm
1.67
0.95
1.10
1.09
3.00
0.78
0.78
2.58
3.22


STANDARD CARBON PARAMETERS
exp3 s2pul
SAMPLE
date May 29 2009
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500c/schreiber/WAN~
G/WYKELN4028_13C.f~
1d
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29986.3
fb not used
bs 8
tpwr 55
pw 3.7
d1 2.000
tof 2000.0
nt 1000
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1030.6
wp 29995.3
vs 29
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10769.8
rfp 9678.3
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 12906
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
HO
HO
SiMe2Ph
N
Ts (±)
56
220
200
180
160
140
120
100
80
60
40
20
ppm

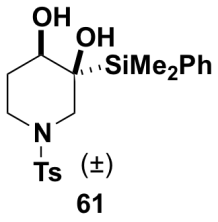

MJIM_4092
exp1 s2pul
SAMPLE
date Jul 8 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 58
pw 5.0
d1 2.000
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 377.53
rfl 5131.3
rfp 3631.3
th 1
ins 3.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
HO
HO
Si^{t}BuMe$_2$
N
Ts
(±)
57
9
8
7
6
5
4
3
2
1
0
ppm
1.79
1.81
1.05
1.07
2.13
1.07
0.93
3.00
0.93
9.51
2.87
2.87


MJIM_4092_13C
exp2 s2pul
SAMPLE
date Jul 8 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 125.781
tn C13
at 1.170
np 65536
sw 28001.4
fb 15000
bs 8
tpwr 57
pw 8.0
d1 3.000
tof 0
nt 1000
ct 424
alock n
gain 56
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2083.6
wp 28000.5
vs 107
sc 0
wc 250
hzmm 112.00
is 500.00
rfl 11768.7
rfp 9684.2
th 13
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 15970
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
HO
HO
Si^{t}BuMe$_2$
N
Ts
(±)
57
200
180
160
140
120
100
80
60
40
20
0
ppm

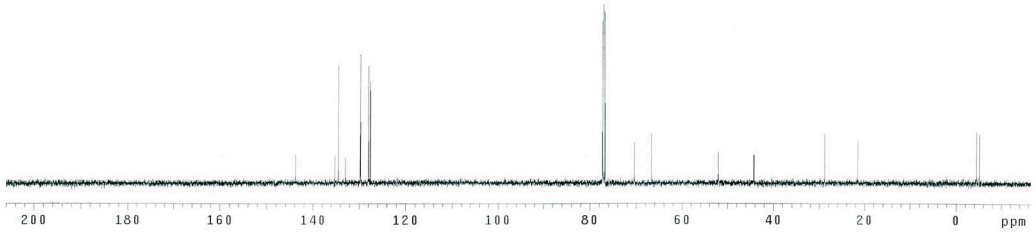

WYKELN4029
exp2 s2pul
SAMPLE
date May 28 2009
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500b/schreiber/WAN~
G/WYKELN4029.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 58
pw 5.0
d1 1.000
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 95.68
rfl 5130.9
rfp 3631.3
th 4
ins 2.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
O
N
Ts
60
9 8 7 6 5 4 3 2 1 0 ppm
1.45 1.54 2.00 1.91 1.96 2.69


WYKELN4047_1H
exp1 s2pul
SAMPLE
date Jun 11 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 499.611
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 54
pw 6.0
d1 1.000
tof 0
nt 64
ct 64
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 4995.6
vs 43
sc 0
wc 250
hzmm 19.98
is 906.44
rfl 5137.7
rfp 3627.2
th 2
ins 2.000
al ph
DEC. & VT
dfrq 499.611
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 14300
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
OH
OH
SiMe2Ph
N
Ts
(±)
61
9 8 7 6 5 4 3 2 1 0 ppm
1.58 1.57 0.97 3.67 0.77 2.00 2.78
1.37 1.52 1.88 1.01 0.81 2.45

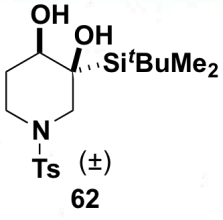

WYKELN4047_13C
exp2 s2pul
SAMPLE
date Jun 11 2009
solvent CDCl3
file exp
ACQUISITION
sfrq 125.781
tn C13
at 1.170
np 65536
sw 28001.4
fb 15000
bs 8
tpwr 57
pw 8.0
dl 2.000
tof 0
nt 1000
ct 408
alock n
gain 56
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2083.6
wp 28000.5
vs 43
sc 0
wc 250
hzmm 112.00
is 500.00
rfl 11768.7
rfp 9684.2
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 15970
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt


OH
OH
SiMe2Ph
N
Ts
(±)

61

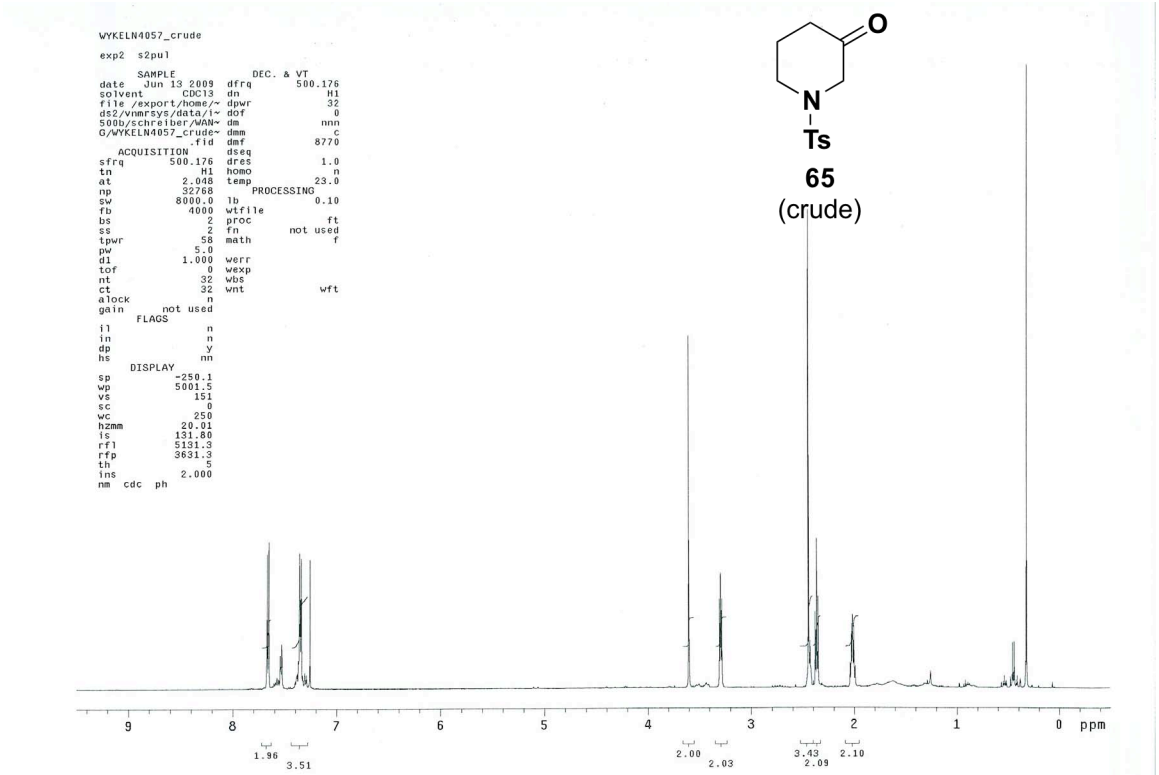

200
180
160
140
120
100
80
60
40
20
0
ppm

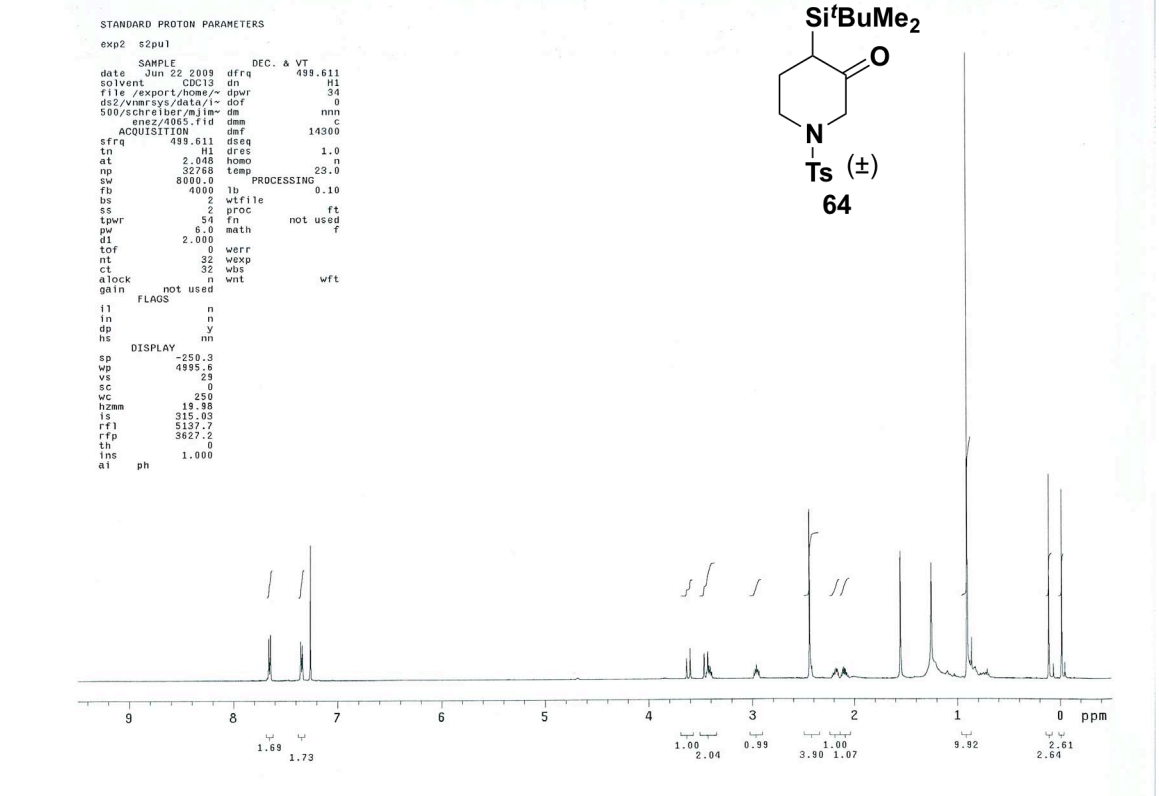

STANDARD PROTON PARAMETERS
exp2 s2pul
SAMPLE
date Jun 18 2009
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500/schreiber/wang~
/MJ4056B_1H.fid
ACQUISITION
sfrq 499.611
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 54
pw 6.0
dl 1.500
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 4995.6
vs 16
sc 0
wc 250
hzmm 19.98
is 124.34
rfl 5137.7
rfp 3627.2
th 0
ins 3.000
ai ph
DEC. & VT
dfrq 499.611
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 14300
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft


OH
OH
SitBuMe2
N
Ts
(±)

62

9
8
7
6
5
4
3
2
1
0
ppm
1.72
1.76
0.99
0.96
1.00
3.00
1.00
1.10
0.87
1.67
8.64
5.81

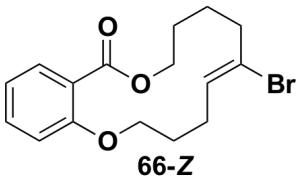

WYKELN4057_crude
exp2 s2pul
SAMPLE
date Jun 13 2009
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500b/schreiber/WAN~
G/WYKELN4057_crude~
.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 58
pw 5.0
d1 1.000
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 131.80
rfl 5131.3
rfp 3631.3
th 5
ins 2.000
nm cdc ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
O
N
Ts
65
(crude)
9 8 7 6 5 4 3 2 1 0 ppm
1.96 3.51 2.00 2.03 3.43 2.09 2.10


STANDARD PROTON PARAMETERS
exp2 s2pul
SAMPLE
date Jun 22 2009
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500/schreiber/mjm~
enez/4065.fid
ACQUISITION
sfrq 499.611
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 54
pw 6.0
d1 2.000
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 4995.6
vs 29
sc 0
wc 250
hzmm 19.98
is 315.03
rfl 5137.7
rfp 3627.2
th 0
ins 1.000
ai ph
DEC. & VT
dfrq 499.611
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 14300
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
SitBuMe2
O
N
Ts (±)
64
9 8 7 6 5 4 3 2 1 0 ppm
1.69 1.73 1.00 2.04 0.99 1.00 3.90 1.07 9.92 2.61 2.64

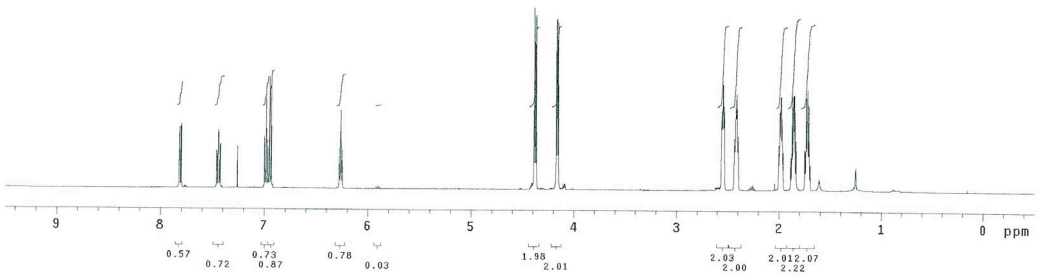
WYKELN16021_1H

exp1 s2pul

SAMPLE		DEC. & VT	
date	Aug 4 2011	dfrq	499.611
solvent	CDCl3	dn	H1
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.611	dm	nnn
tn	H1	dmm	c
at	2.048	dmf	14300
np	32768	dseq	
sw	8000.0	dres	1.0
fb	4000	homo	n
bs	4	temp	23.0
ss	2	PROCESSING	
tpwr	54	lb	0.10
pw	6.0	wtfile	
d1	0.300	proc	ft
tof	0	fn	not used
nt	32	math	f
ct	32		
alock	n	werr	
gain	not used	wexp	
FLAGS		wbs	
il	n	wnt	wft
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.3		
wp	4995.6		
vs	75		
sc	0		
wc	250		
hzmm	19.98		
is	569.97		
rfl	5137.7		
rfp	3627.2		
th	3		
ins	2.000		
ai ph			



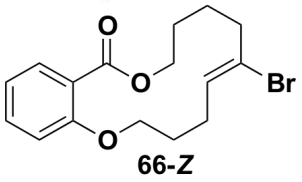
66-*Z*



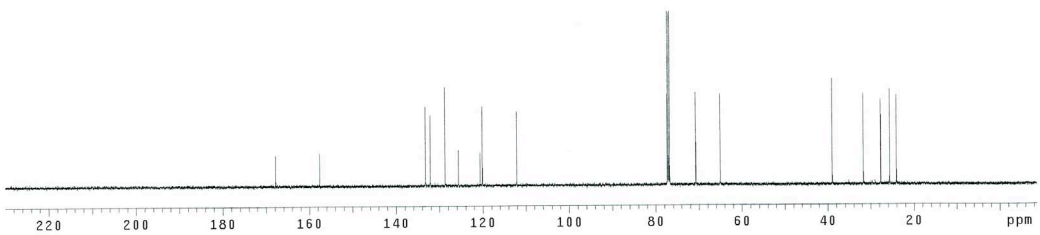
WYKELN16021_13C

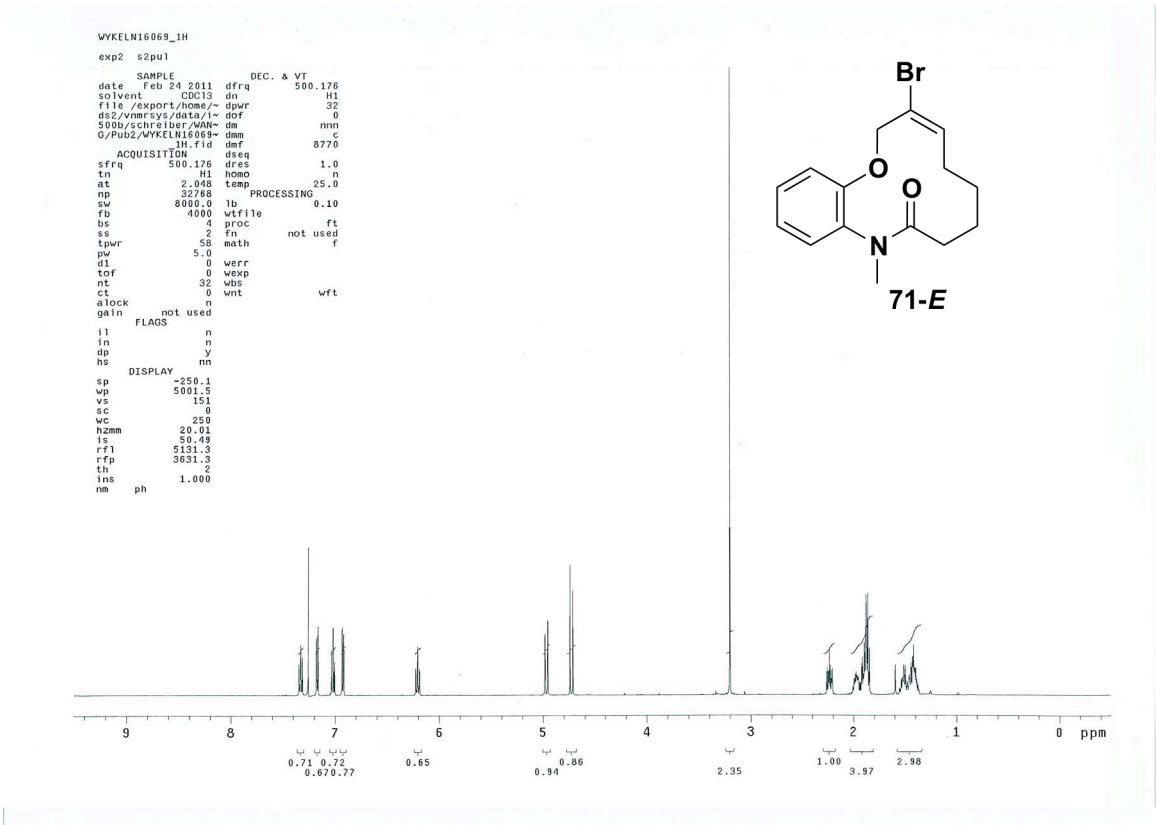
exp1 s2pul

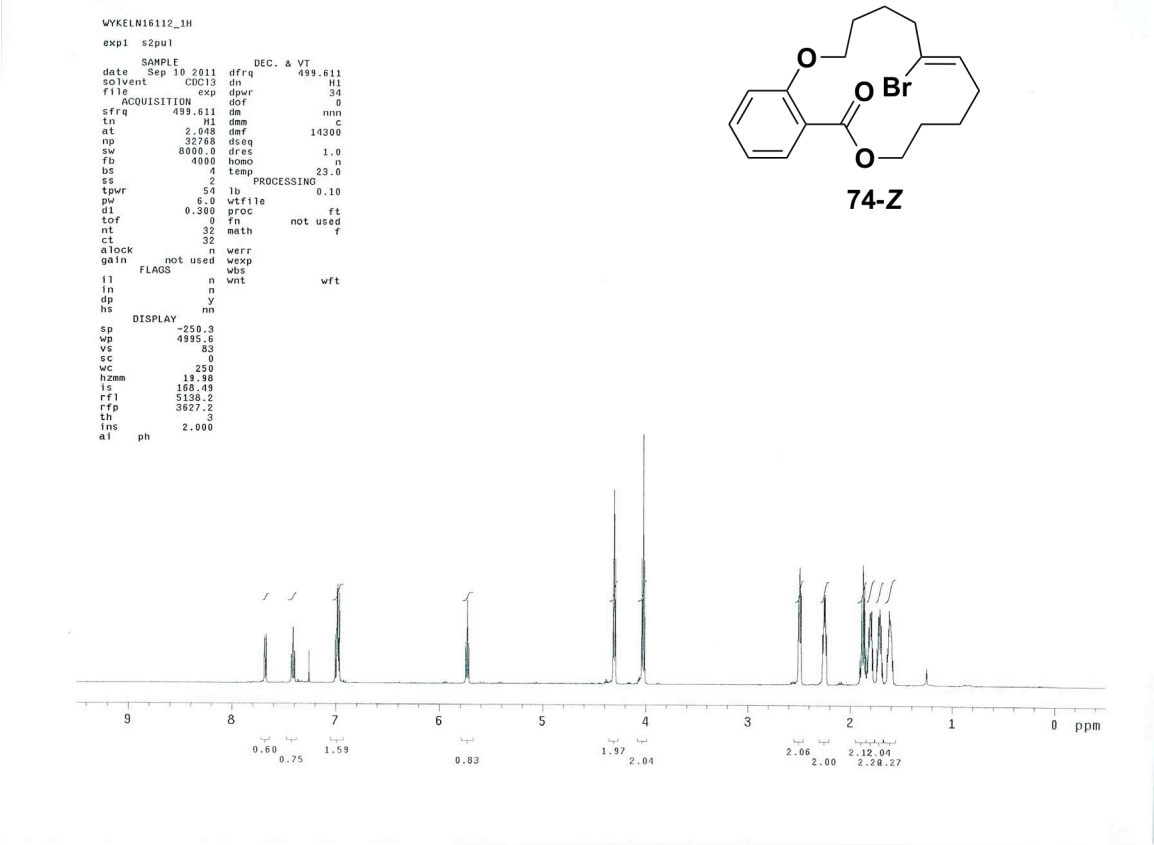
SAMPLE		DEC. & VT	
date	Aug 4 2011	dfrq	499.874
solvent	CDCl3	dn	H1
file	exp	dpwr	48
ACQUISITION		dof	0
sfrq	125.707	dm	yyy
tn	C13	dmm	w
at	1.092	dmf	8929
np	65536	dseq	
sw	29996.3	dres	1.0
fb	not used	homo	n
bs	16	temp	25.0
tpwr	55	DEC2	
pw	4.8	dfrq2	0
d1	0	dn2	
tof	2000.0	dpwr2	1
nt	99999	dof2	0
ct	848	dm2	n
alock	n	dmm2	c
gain	not used	dmf2	10000
FLAGS		dseq2	
il	n	dres2	1.0
in	n	homo2	n
dp	y	DEC3	
hs	nn	dfrq3	0
DISPLAY		dn3	
sp	-1089.7	dpwr3	1
wp	29995.3	dof3	0
vs	42	dm3	n
sc	0	dmm3	c
wc	250	dmf3	10000
hzmm	119.98	dseq3	
is	500.00	dres3	1.0
rfl	10768.9	homo3	n
rfp	9678.3	PROCESSING	
th	5	lb	1.00
ins	100.000	wtfile	
nm cdc ph		proc	ft
		fn	not used
		math	f
		werr	
		wexp	
		wbs	
		wnt	



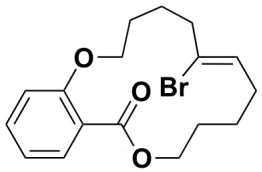
66-*Z*



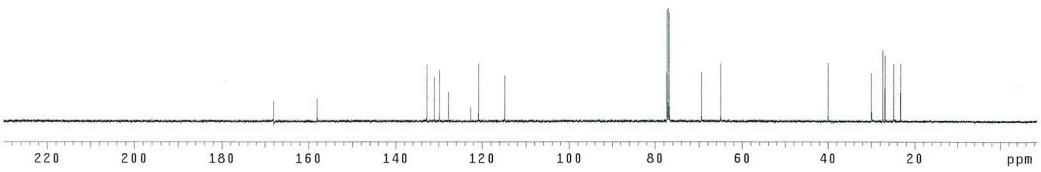

WYKELN16069_1H
exp2 s2pul
SAMPLE
date Feb 24 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/1~
500b/schreiber/WAN~
G/Pub2/WYKELN16069~
1H.fid
ACQUISITION
sfrq 500.176
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5001.5
vs 151
sc 0
wc 250
hzmm 20.01
is 50.49
rfl 5131.3
rfp 3631.3
th 2
ins 1.000
nm ph
DEC. & VT
dfrq 500.176
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 8770
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
Br
O
O
N
71-E
9
8
7
6
5
4
3
2
1
0 ppm
0.71 0.72
0.67 0.77
0.65
0.94
0.86
2.35
1.00
3.97
2.98


WYKELN16112_1H
exp1 s2pul
SAMPLE
date Sep 10 2011
solvent CDCl3
file exp
ACQUISITION
sfrq 499.611
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.3
wp 4995.6
vs 83
sc 0
wc 250
hzmm 19.98
is 168.49
rfl 5138.2
rfp 3627.2
th 3
ins 2.000
al ph
DEC. & VT
dfrq 499.611
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 14300
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
O
O
Br
O
74-Z
9
8
7
6
5
4
3
2
1
0 ppm
0.60
0.75
1.59
0.83
1.97
2.04
2.06
2.00
2.12.04
2.28.27

```
WYKELN16112_13C

exp2  s2pul

      SAMPLE
date   Sep 10 2011
solvent      CDCl3
file          exp
    ACQUISITION
sfrq       125.707
tn             C13
at             1.092
np             65536
sw          29996.3
fb          not used
bs                16
tpwr              55
pw               4.8
d1                 0
tof           2000.0
nt             99999
ct               624
alock              n
gain        not used
      FLAGS
il                 n
in                 n
dp                 y
hs                nn
     DISPLAY
sp           -1089.7
wp           29995.3
vs                27
sc                 0
wc               250
hzmm          119.98
is            500.00
rfl          10768.9
rfp           9678.3
th                 3
ins           100.000
nm  cdc  ph

          DEC. & VT
dfrq         499.874
dn                H1
dpwr              48
dof                0
dm               yyy
dmm                w
dmf             8929
dseq
dres             1.0
homo               n
temp            25.0
          DEC2
dfrq2              0
dn2
dpwr2              1
dof2               0
dm2                n
dmm2               c
dmf2           10000
dseq2
dres2            1.0
homo2              n
          DEC3
dfrq3              0
dn3
dpwr3              1
dof3               0
dm3                n
dmm3               c
dmf3           10000
dseq3
dres3            1.0
homo3              n
     PROCESSING
lb              1.00
wtfile
proc               ft
fn          not used
math               f

werr
wexp
wbs
wnt
```



74-*Z*

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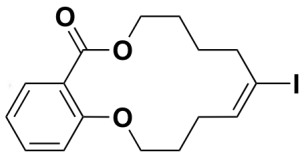

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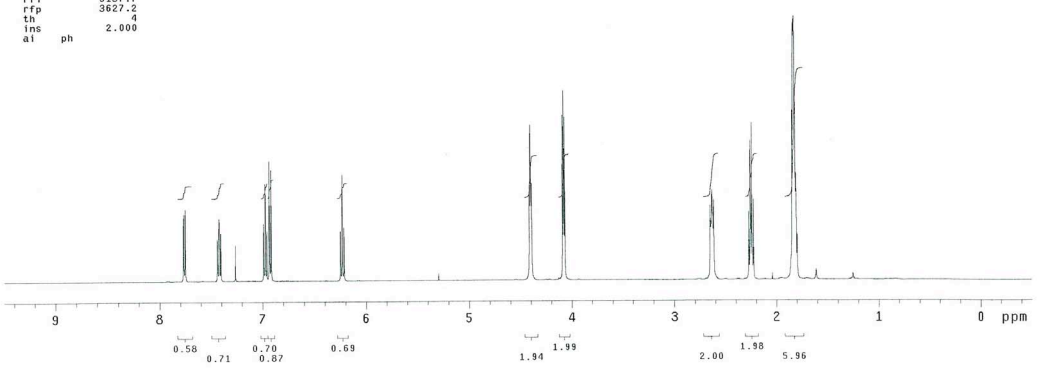

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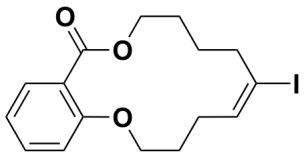

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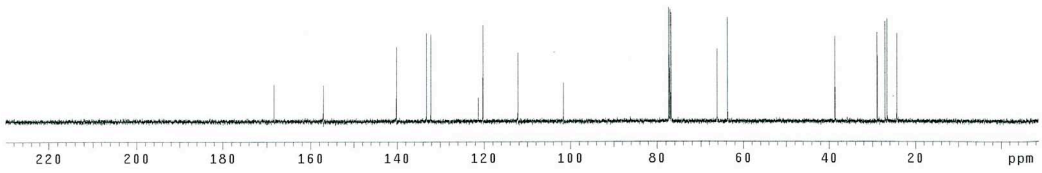

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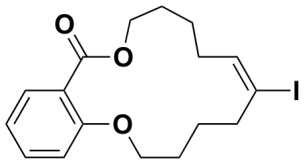

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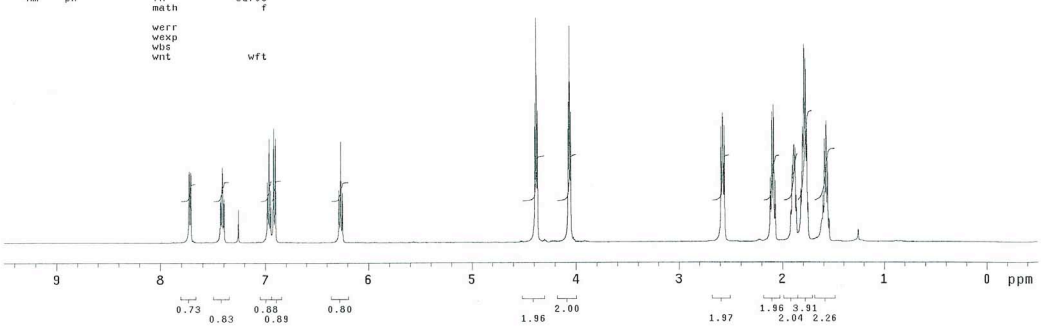

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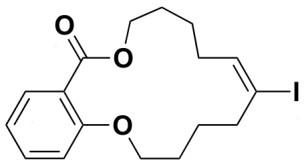

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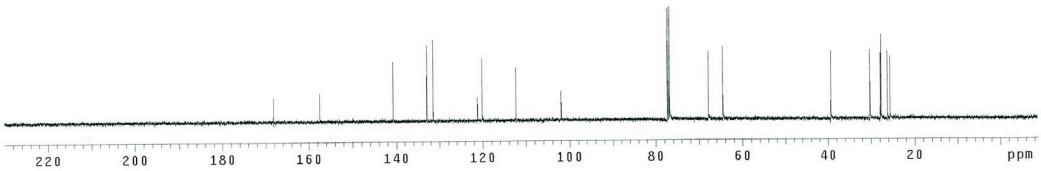

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FLAGS			
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dp	y		
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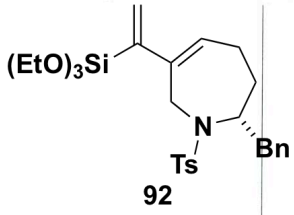
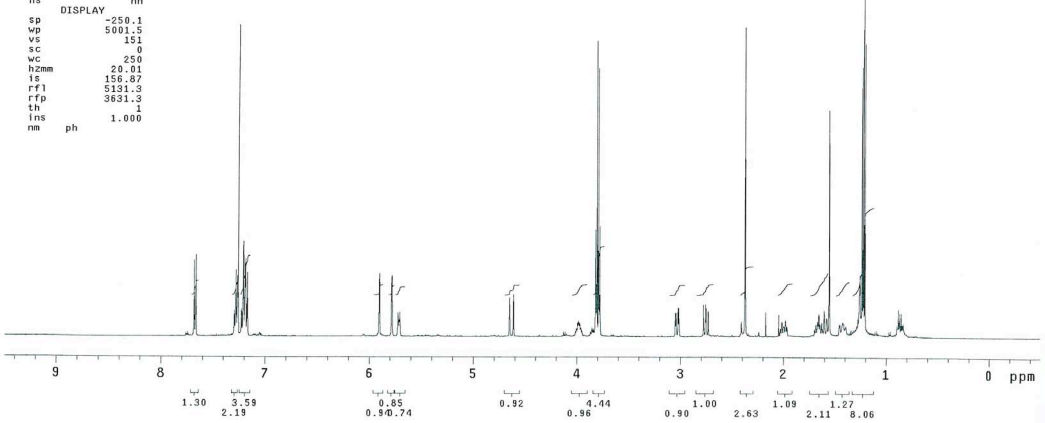
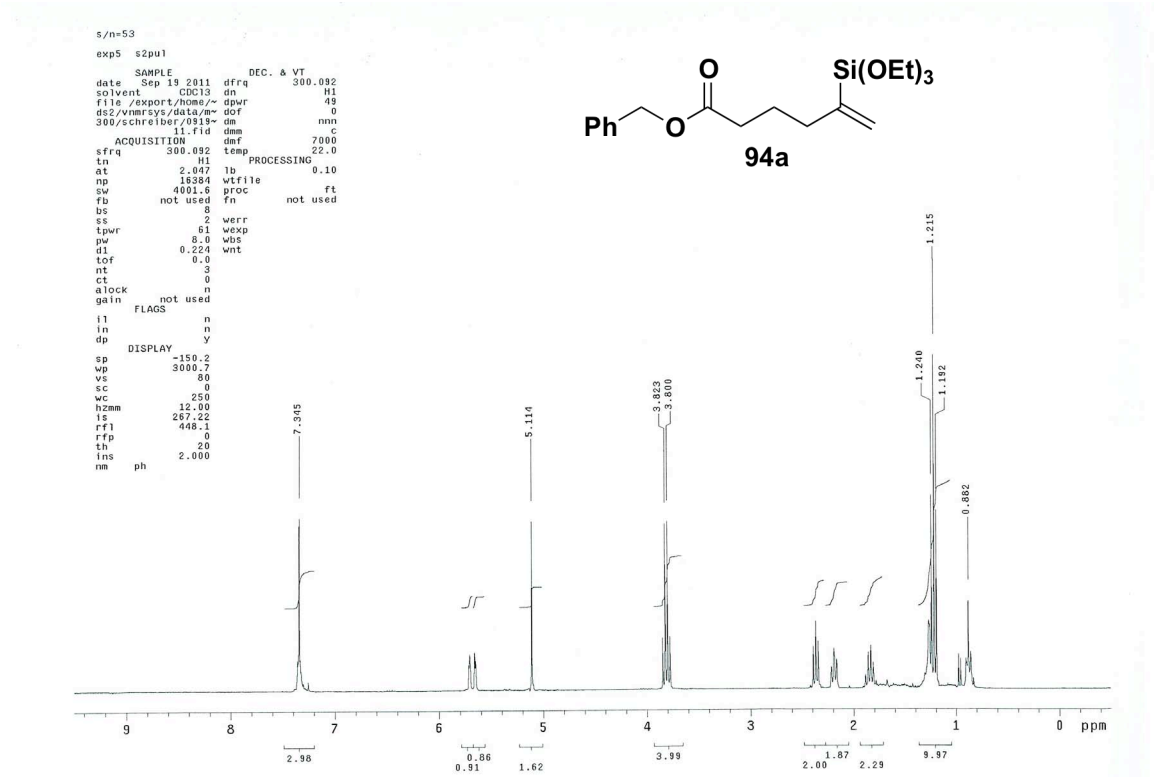
nm ph			



92

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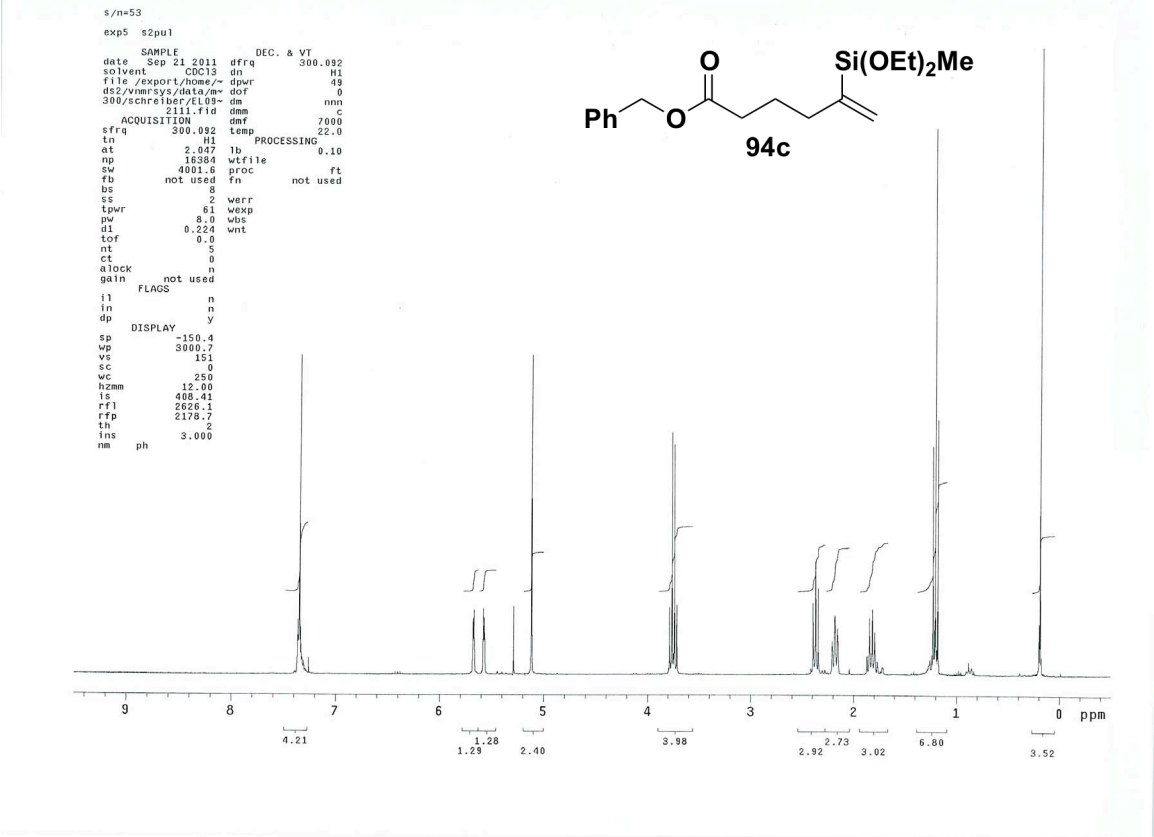
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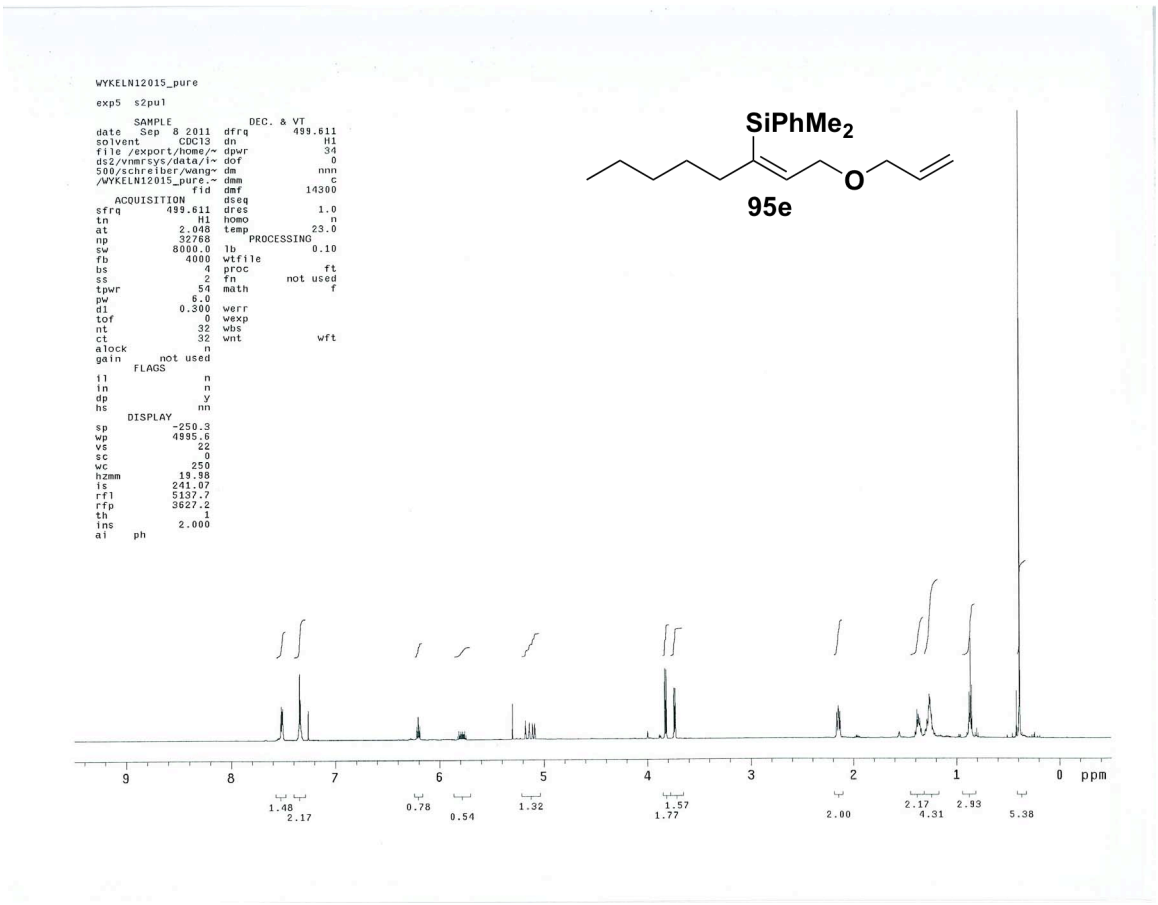
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Chapter II.

Synthesis of Diversity-Oriented Synthetic Fragment Library and Biological Screening against GSK3β

Chapter II-1. Introduction

The use of small-molecule probes to shed light on both normal and disease-associated biological phenomena is a powerful approach in chemical biology.[1-4] With respect to disease biology, such probes serve as useful starting points to produce new medicines. Technological advances have made high-throughput screening (HTS) the predominant mechanism through which these probes are discovered.[5-11] The success of such an approach is inextricably linked to the identity and the quality of the screening collection.[12,13] Synthetic organic chemistry has played a pivotal role in generating large collections of small molecules to be screened in various HTS campaigns. However, even the largest conceivable compound collections have fallen far short of sampling the chemical diversity space (an estimated to be upward of 10^{60} molecules containing up to 30 non-hydrogen atoms).[14] Compounding the problem is the fact that most small molecule screening collections have substantial overlap, leading to a dearth of new chemical entities being discovered.[15,16] Clearly, sources of chemicals with greater diversity are needed and alternative approaches toward probe development are warranted.

Fragment-based drug discovery (FBDD) is a complementary strategy to HTS, and is a well-validated approach toward generating small-molecule leads.[17-23] The central theme underlying FBDD is the screening of a library of low molecular weight compounds (typically less than 250 g/mol),[24] or "fragments," against a specific biological target. The number of potential fragments with up to 12 heavy atoms (not including three- and four-membered ring structures) has been estimated at 10^{7}.[25] As a result, fragment libraries though substantially smaller, are still able to sample a higher percentage of the chemical

space compared to HTS screening collections.[24-26] Because fragment molecules are small in size, they typically bind with lower affinity to a target protein (micromolar to millimolar range) compared with drug-like molecules (nanomolar to micromolar range). Consequently, the binding of a fragments is mostly captured by very sensitive biophysical techniques capable of picking up such weak interactions.[27] Although the binding affinity of a fragment is low, it usually has high ligand efficiency which makes it a good starting point.[21] After an appropriate fragment hit has been identified, it then serves as a constructive chemical anchor for the generation of a more potent ligand. This can be achieved by synthetically "growing" or "linking" the bound fragments.[28-35] FBDD approaches are most efficiently executed when an X-ray or NMR structure of the target is available, giving critical binding information.[36-45] With structural information in hand, follow-up chemistry is guided in a rational manner requiring fewer analogs to be made toward a potent lead compound.

The increasing popularity of fragment-based screening has led to an increase in the number of commercial vendors selling fragments. However, most fragment libraries used to date have been limited to aromatic heterocycles with an underrepresentation of chiral, enantiopure sp^3-rich compounds.[46] These traditional planar sp^2-rich fragments have undoubtedly led to the generation of unique and high-quality starting points.[22,47,48] In order to explore more difficult biological targets without well-defined binding pockets (*e.g.* transcription factors), more emphasis should be placed upon developing compounds with different structural motifs.

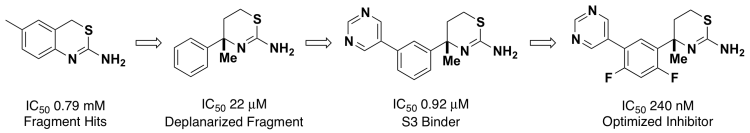
Additionally, there have been several recent studies demonstrating the benefits of increasing the saturation content in drug-like compounds.[49-51] The increased sp^2 content of a molecule was found to negatively correlate with the aqueous solubility, while positively correlating with lipophilicity, serum albumin binding, and CyP450 inhibition, suggesting that drug candidates with fewer aromatic rings were more "developable" than the lead compounds with more aromatic rings.[50] The importance of sp^3-rich lead compounds in these studies can be extended to fragments, which support the hypothesis that sp^3-rich fragments can serve as higher-quality starting points in terms of physicochemical properties.

In addition to insufficient chemical diversity, buying fragments from various commercial vendors does not allow for efficient structure-activity relationship (SAR) determination. Because compounds were not selected on the basis of synthetic availability of their analogs, the chemistry to optimize hits from commercial collections can often be challenging and problematic. However, through proactively synthesizing a fragment collection, analogues with different regiochemical, stereochemical, and skeletal properties can be easily accessed to facilitate a rapid optimization after the primary screen.

The modification of fragments is another important step in the entire FBDD process. Guided by the structural information of the fragment binding against the macromolecule, positions and directions for "growing" or "linking" can be determined. The growth vector from sp^2 atoms (carbon or nitrogen) of traditional planar fragments is confined to the

plane of the ring. On the contrary, sp^3 atoms provide different geometric vectors off of a fragment, which enables orientation-dependent modifications of fragments into pockets of an active site that might otherwise be inaccessible to planar aromatic fragments. Researchers at Eli Lilly have recently demonstrated this notion (Figure **II-1**) by showing that the rigid bicyclic scaffold benzothiazine failed to afford optimal vectors for fragment growth into an adjacent pocket.[52] The problem was solved by deplanarizing the aminothiazine, and introducing a quaternary methyl group to both exploit this topology and enhance chemical stability.

Figure II-1. Deplanarization of bicyclic fragment to enhance occupancy of S1 pocket of BACE1 and provide vector for introduction of an S3 binding element to increase affinity.[52]



Taken together, these examples sufficiently show the benefits of putting an upfront effort into the synthesis of a diverse fragment collection. A fragment collection comprised of molecules that can be accessed using modular syntheses would circumvent downstream challenges. In an effort to generate such a library, a diversity-oriented synthesis (DOS) approach was undertaken.

After several years of exploration in the area of DOS, a build/couple/pair strategy (B/C/P) has recently emerged, which has been proven successful in producing molecules suitable

for HTS.[53-69] In a recent paper, Dr. Alvin W. Hung, Mr. Alex Ramek, and I have demonstrated the application of this concept toward the generation of low molecular weight fragments. Short and efficient synthetic pathways following the logic of B/C/P were used to generate fragments that were structurally diverse and rich in sp^3-content.

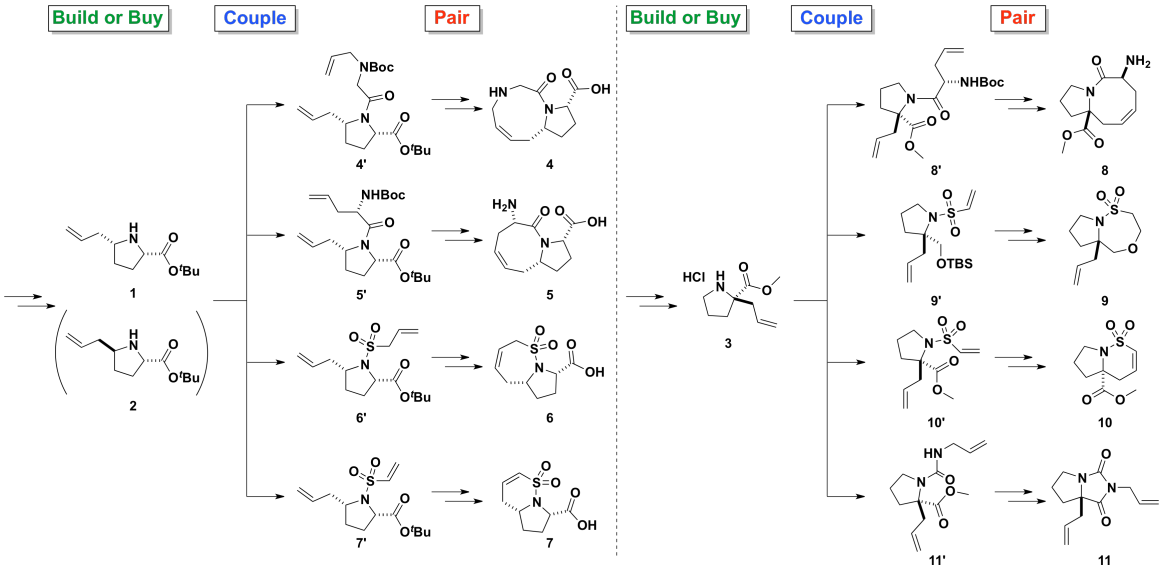
In addition to shape diversity and higher sp^3 content, the notion of synthetic accessibility of analogues was also incorporated into the design of fragments. In an ideal situation, one would like to have the ability of making modifications at every single atom of the scaffold. To achieve this goal, special attention was paid toward the synthetic accessibility and commercial availability of derivatives of the starting building blocks. Functional groups that have the potential to be diversified are also incorporated (see Chapter **II-2-2**). Another advantage of generating DOS fragments from the B/C/P strategy is the potential access to all possible stereoisomers including enantiomers and diastereomers in their enantiopure forms. Such a fragment library would enable the exploration of stereochemical structure-activity relationships, and more importantly allow for the differentiation between specific binders versus nonspecific binders. Such information is not included in commercial vendor collections.

Chapter II-2. Design and Synthesis of Diversity-Oriented Synthetic Fragment Libraries

1. Proline-based fragment library

Together with Dr. Alvin Hung, we designed a synthetic pathway starting with proline building blocks **1-3** (Scheme **II-1**). One factor for selecting these compounds was the readily available enantiomerically pure versions of all stereoisomers.[70-72] Another benefit of using proline building blocks includes the extensive amount of chemistry focusing on the generation of pyrrolidine-based scaffolds.[73] This information is constructive given that, if binders are found, numerous substituted pyrrolidines can be generated in the follow-up chemistry phase from a variety of known methods.

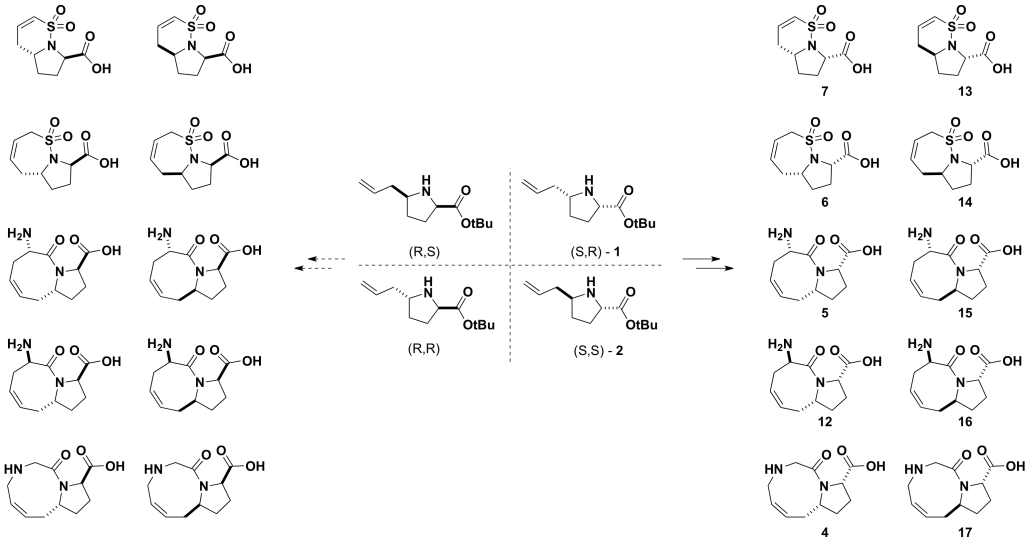
Scheme II-1. Application of a B/C/P approach to make bicyclic compounds starting from building blocks **1-3**.



With compounds **1-3** in hand, we proceeded to the couple and pair phases of our

pathway. Scheme **II-1** illustrates the implementation of this strategy. Intermolecular coupling reactions based around the building blocks yielded more densely functionalized pyrrolidine molecules (compounds **4'-11'**),[70,74,75] which were then paired under various conditions such as RCM, lactam formation, Michael addition, etc. Skeletally diverse bicyclic fragments that have 5,5, 5,6, 5,7, 5,8, and 5,9 fused ring systems were generated.

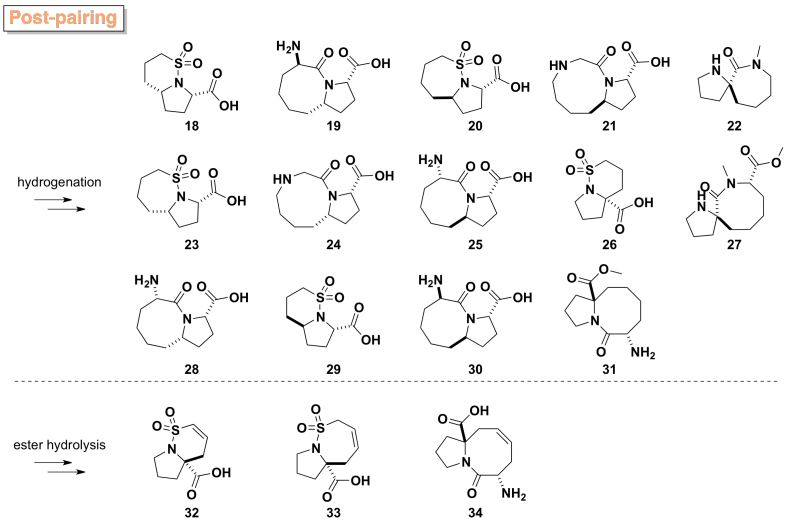
Scheme II-2. Using a B/C/P approach to obtain the full matrix of all possible diastereomeric products.



The devised B/C/P strategy not only created a small library of fragments of diverse skeletal structures, but also one rich in stereochemical variation. The mixing and matching of various stereogenic building blocks followed by versatile RCM pairing reactions generated a complete set of all possible diastereomers (Scheme **II-2**). The difference between various stereoisomers might be significantly large enough to completely obliterate binding. Therefore having a complete set of stereoisomers would facilitate the identification of the more potent stereoisomer and provided insights on

further design of a better inhibitor.

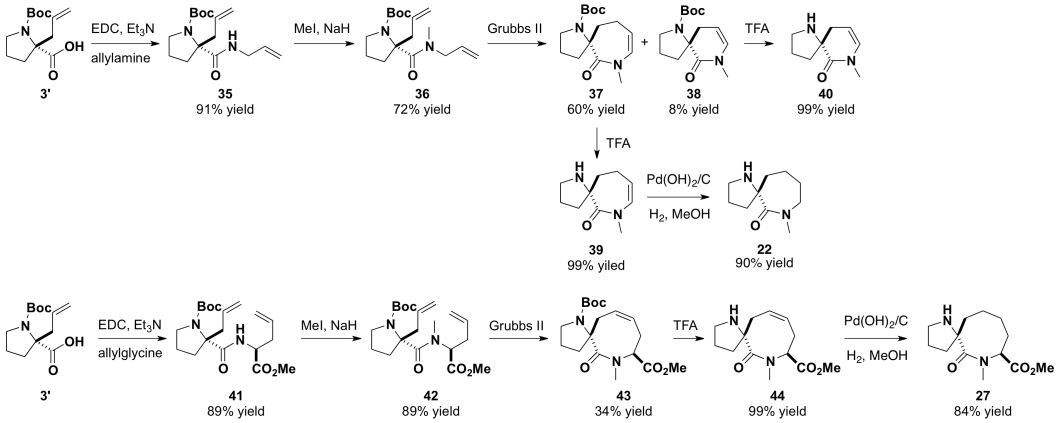
Scheme II-3. Reducing the olefin groups in a post-pairing phase to generate a new set of fragments.



In addition to structural and stereochemical diversity, we designed a third diversity element into our library: a "postpairing phase". Fragments, because of their low molecular weight usually display weak binding affinities. Consequently, the particular functional groups within a given fragment are critical to the observation of a binding event. Subtle changes in functionalities and shape of fragments can result in significant changes to binding affinities. Accordingly, we determined that it would be imperative to take the scaffolds that were assembled in the B/C/P strategy and perform functional group interconversion reactions on them to produce new fragments (Scheme **II-3**). The result of these modifications would be to generate "functional group diversity" within the fragment library. Methyl esters were hydrolyzed to the carboxylic acids to give fragments **32**, **33**, and **34**. These functional interconversions would have a significant impact on the

overall electronic properties of the fragments. The reduction of olefins in the fragments was also performed (Scheme **II-3**), resulting in increased sp^3 carbon atom content and a different conformational profile for the reduced fragments.

Scheme II-4. Synthesis of spirocyclic compounds.



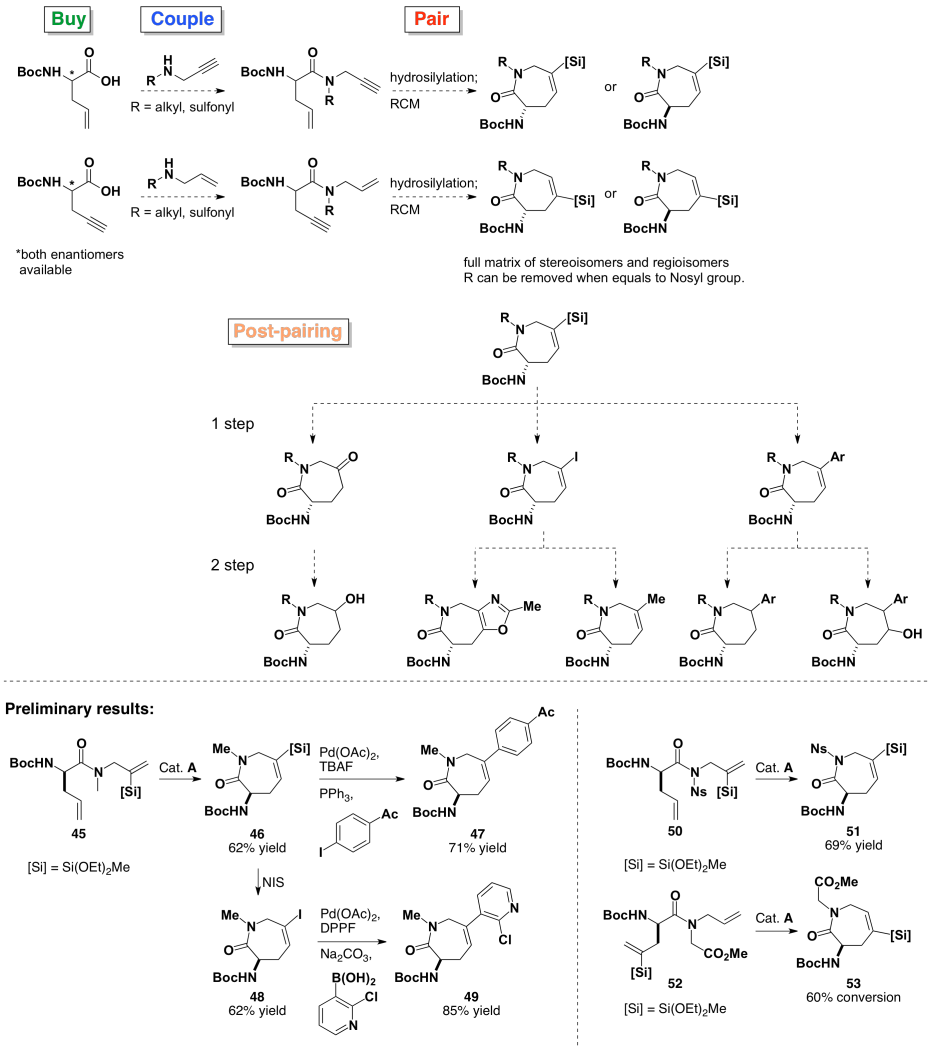
Besides the design of the proline-based fragment library, my contribution to the execution of the synthesis was focused on the generation of spirocyclic fragments. Commercially available starting material **3'** (derivative of compound **3**, see Scheme **II-1**) was coupled with allylamine (Scheme **II-4**). The RCM of **35** failed to generate the cyclized product because the thermodynamically favored rotamer of the secondary amide causes the two allyl groups to be positioned away from each other. To overcome this problem, **35** was methylated yielding the tertiary amide **36**, which allowed for the two rotamers to be isothermic and interconvertable. The subsequent RCM of **36** gave rise to two enamides, a major product **37** and a minor product **38**. In both products, migration of the double bond was observed, which is indicative of isomerization during the RCM reaction, presumably catalyzed by ruthenium hydride species.[76,77] Formation of the 6-

membered enamide **38** can be rationalized on grounds that the migration of the double bond occurred before the RCM releasing propene (instead of ethylene) to generate **38**. However, migration of the double bond *in situ* could happen in the RCM of tertiary amide **42**, but was not extensively studied. The desired spirocyclic product **43** was obtained with moderate yield (Scheme **II-4**).

2. Fragment library based on RCM of vinylsiloxanes

In addition to the proline-based fragment library mentioned above, a fragment library focusing on nitrogen-containing heterocycles was designed taking advantages of the RCM of vinylsiloxanes. The synthetic pathway (Scheme **II-5**) started from both enantiomers of allylglycine and propargylglycine, which are commercially available. Coupling of the Boc-protected amino acids with the corresponding propargylamine or allylamine gave rise to the tertiary amide with both alkene and alkyne functionality in it. After hydrosilylation of the alkyne, the vinylsiloxanes were subjected to the optimized RCM conditions described in Chapter **I-2-2**. The R group must be an alkyl group or sulfonyl group for the RCM reaction to orrur. The presence of a N-aryl group did not permit RCM. It is rational that the N,N-phenylalkyl amide will adopt a different conformation than a N,N-bisalkyl amide, which may cause the dramatic change in the rates of the ring-closing reaction. If a *m*-nitrophenylsulfonyl (nosyl) group is used, it can be removed to release the secondary amide that has different hydrogen bonding ability compared to the sulfonamide or the tertiary amide. The switch between the alkene and alkyne enables the incorporation of silyl groups at either of the two sp^2-olefinic carbons in the RCM product so that both regioisomers are accessible.

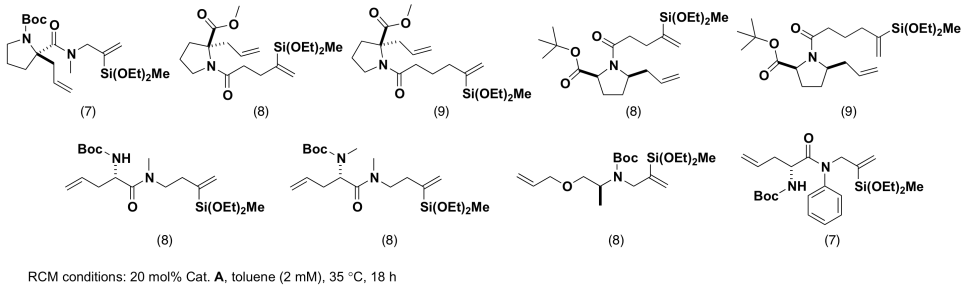
Scheme II-5. Proposed synthetic pathway towards a 7-membered nitrogen-containing fragment library starting from amino acids and preliminary results.



Once the RCM product was obtained, a one-step transformation of the alkenylsiloxane moiety yielded either the ketone, alkenyl iodide, or the aryl-substituted alkene. Furthermore, an additional step would generate different functionalities from the parent fragments such as the secondary alcohol, substituted oxazole,[78] or the saturated version of the 7-membered ring. Preliminary results have shown that both regioisomers **45** and **52**

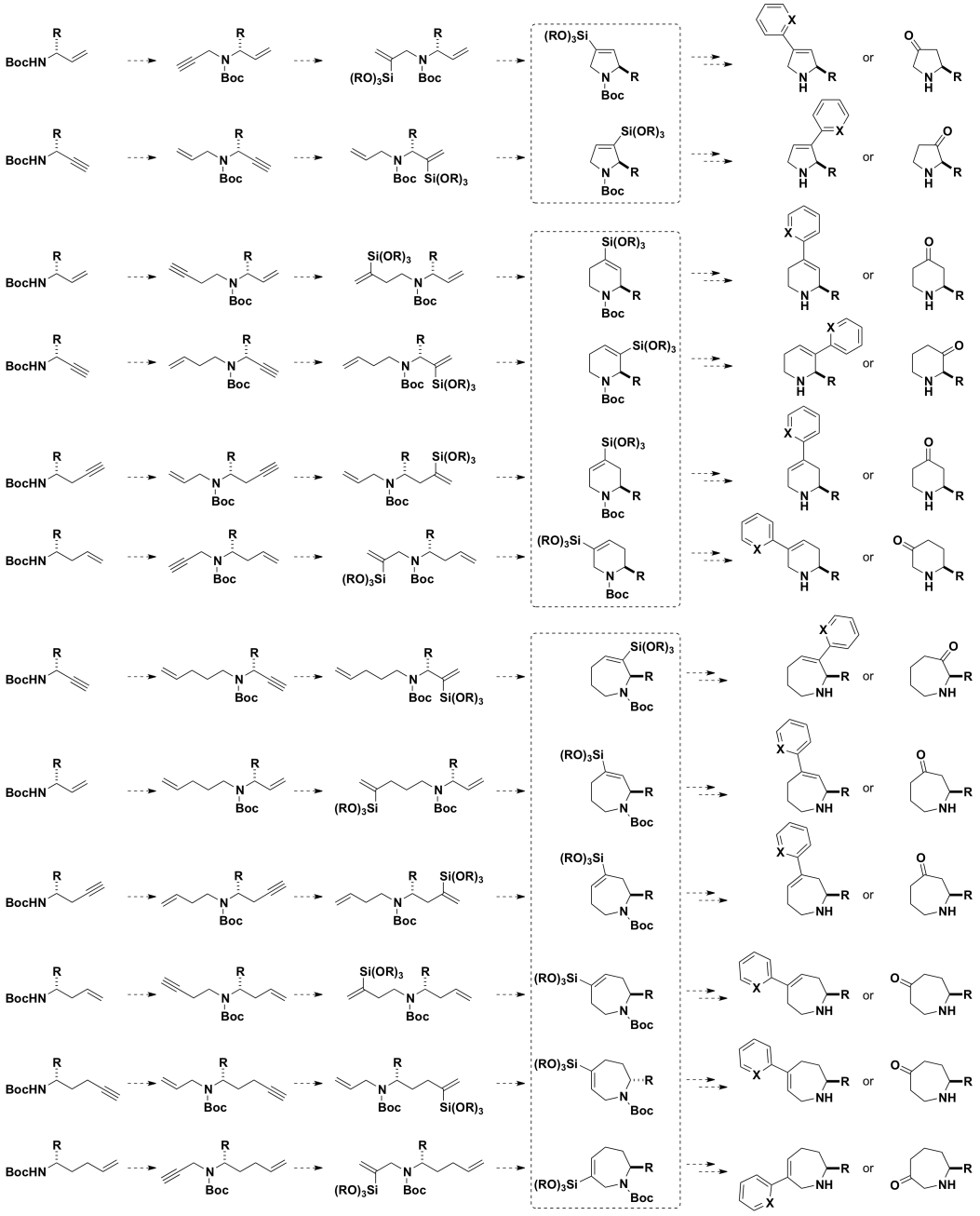
can be closed successfully with similar reaction outcome (Scheme **II-5**). Subsequent cross-coupling reactions can be executed from product **46** directly using Hiyama coupling[79] or from the alkenyl iodide **48** using Suzuki coupling.[80] In addition, the nosyl-protected amide **50** afforded the cyclized product with good yield. The synthesis of this library is currently being performed by Mr. Evan Liang.

Figure II-2. Substrates that failed to be closed under optimal RCM conditions (ring sizes of the desired products in parentheses).



To understand the generality of building up libraries around alkene- or alkyne-containing amino acids and amino alcohols, several other substrates were also prepared and subjected to the optimal RCM conditions. However, proline-bsaed vinylsiloxanes failed to generate the 7- to 9-membered products with a conversion larger than 5% (Figure **II-2**, first row). Substrates based on protected allyl glycines or amino alcohols to provide 8-membered products also failed to be cyclized (Figure **II-2**, second row). This reflects the challenge of cyclizing medium size rings from 7- to 9-members due to high intrinsic ring strain as well as the constraint of the introduction of the silyl group.

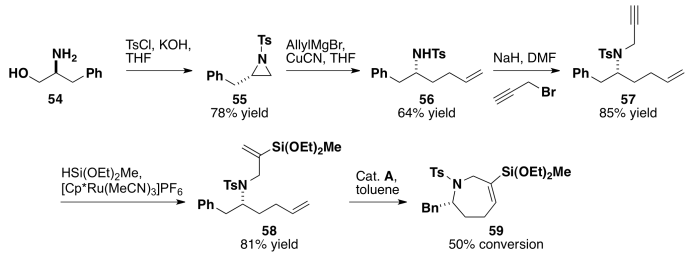
Scheme II-6. Proposed synthetic pathway towards a nitrogen-containing fragment library starting from chiral amines.



Although the RCM of vinylsiloxanes to form rings larger than 7 is dependent on the nature of the substrates, it has been shown that the reaction is quite general towards the

formation of 5- and 6-membered rings in Chapter **I-1-4** and **I-2-1**. We designed another pathway to access a diverse set of linked-bicyclic compounds and cyclic ketones with different ring sizes, stereoisomers, regioisomers, and various aromatic groups (Scheme **II-6**). Though the complete set of proposed 7-membered rings may not be fully accessible, I have explored the synthesis of **59** to test the feasibility of this approach (Scheme **II-7**). Starting with the (*S*)-amino alcohol **54**, the tosyl-protected aziridine **55** was obtained in a one-pot transformation. The aziridine **55** was then opened with allylcyanocuprate reagent to install the terminal alkene. Propargylation of compound **56** gave rise to the alkenyl alkyne **57** with excellent yield. Hydrosilylation and RCM of **57** completed the synthesis of 7-membered alkenylsiloxane **59** in acceptable yields. The other starting chiral amines shown in Scheme **II-6** are either commercially available or easily accessible from ring opening of chiral aziridines following the similar route to compound **56**.

Scheme II-7. Preliminary results on RCM to form a 7-membered product.



Chapter II-3. Screen the Synthetic Fragment Library against GSK3β

1. Initial biophysical screening using thermal shift assay

The glycogen synthase kinase (GSK3β) was selected as the proof-of-concept target for screening the DOS fragments. GSK3β is a well-characterized target that is involved in a range of developmental and homeostatic cellular biology. Signaling abnormalities in the pathway involving this protein have been linked to a variety of human diseases. Pertaining to neuropsychiatric disease, growing evidence from human genetic studies implicates aberrant GSK3β signaling, including the discovery of the schizophrenia risk gene DISC1 as a direct binder and inhibitor of GSK3β,[81] and the bHLH transcription factor TCF4 (ITF-2) as a GSK3β/B-catenin target gene[82] making it a target of interest within the Stanley Center for Psychiatric Disease at the Broad Institute. To convincingly portray the role of GSK3β in neuropsychiatric disorders, a small-molecule ligand with exquisite potency and selectivity is required. To date, it has been difficult to obtain a small-molecule with such properties based on HTS. Therefore, a fragment-based approach has the potential to be impactful in an area where more conventional methods have not succeeded.

A florescence thermal shift assay[83] was used to screen the entire fragment library against GSK3β. This method of screening has the advantage of robust throughput (96 well per 0.5 hour), enabling it for use as a primary screen against GSK3β. Our collaborator Dr. Steve Haggarty, of the Stanley Center and the Chemical Biology Platform had extensive

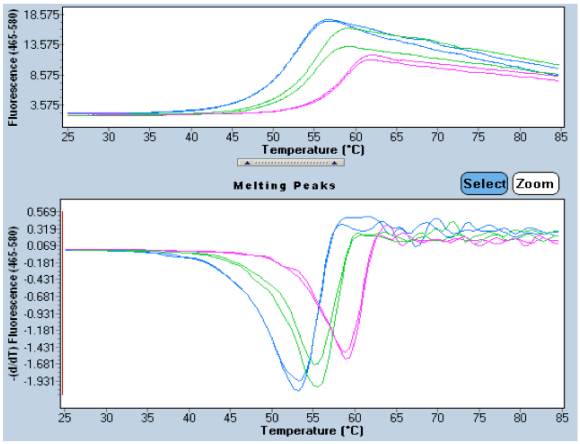
experience on using thermal shift with GSK3β. Accordingly, significant thermal shifts of 6-8 °C had been observed by them for known (nonselective) inhibitors of GSK3β. This would be beneficial, as it would translate into higher sensitivity when screening for fragments.

Optimization of the thermal shift assay against GSK3β was performed together with Dr. Alvin W. Hung and Mr. Alexander Ramek. Different combinations of protein concentration and dye concentration were tested until a good fluorescence curve was obtained with minimal amount of protein. Next the DMSO tolerance of GSK3β was determined. Given that high concentrations of fragment are required for the initial screening, we wanted to use a high percentage of DMSO in order to solubilize the ligand. However, higher concentration of DMSO can also interfere with the protein and eventually denature it. After several experiments, the optimal condition was determined to be 0.12 mg/mL GSK3β, 1:400 dilution of Sypro Orange from the original stock, and 2.5% DMSO. The assay was performed in 384-well plate format with final volume of 5 μL using a buffer solution containing 50 mM HEPES (pH 7.5) and 150 mM NaCl.

Next, known binders of the protein were tested under the optimized assay conditions to determine whether the assay was working as well as its sensitivity. In the GSK3β case, several known inihibitors were tested and all were discovered to give a positive thermal shift (Figure **II-3**). GW8510, an inhibitor of cyclin-dependent kinase-2, also inhibits *T. brucei* GSK-3 short protein with an IC_{50} of 1 nM.[84] When tested at 20 μM, it showed a 6

°C positive thermal shift. Another inhibitor **BRD4003** found by our collaborators, which has a K_D of 130 nM (measured by SPR) also showed a shift around 3 °C. It will be interesting to note the correlation of thermal shift with K_d in future experiments, when the whole set of data is collected.

Figure II-3. Thermal shift experiments on GSK3β with positive controls.



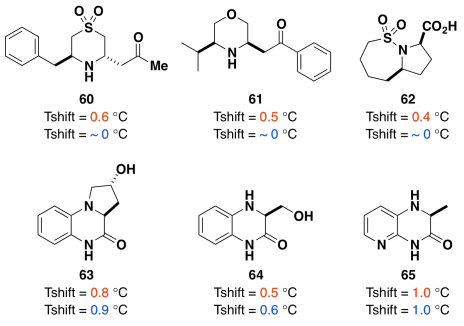
Top traces: fluorescence level over temperature; bottom traces: first derivative of fluorescence level over temperature. Blue: DMSO control; green: compound **BRD4003**; pink: compound **GW8510**.

ATP is a cofactor of GSK3β and can also bind to the protein. As an additional control, we desired to determine whether the binding of ATP would stabilize the protein or not. To our surprise, when tested at 240 μM of ATP, the melting point of the protein was unchanged, suggestive of no interaction. By checking our assay conditions carefully, we found out that the assay buffer did not contain Mg(II), which is required for the activity of the protein. We then retested ATP in the presence of 10 mM $MgCl_2$, and a 2.0 °C

thermal shift was observed. Therefore, Mg(II) is required for ATP binding but not for the positive controls we had tested. We decided to screen our compound collection with and without Mg(II) in order to compare the results.

The screening of our fragment collection without Mg(II) yield 6 compounds that showed a positive thermal shift value larger than 0.4 °C (Figure **II-4**). Compound **60**, **61**, and **62** gave no shift when the assay was performed in the presence of Mg(II). However compound **63**, **64**, and **65** showed slight increases in their shift values when Mg(II) was present. We speculate that Mg(II) binding causes a conformational change of the protein that disfavors the binding of the first 3 compounds but favors the binding of others. This suggests to us that the first three compounds have distinct binding modes that might be interesting to study. However, we decided to follow up with the compounds that bind to the protein both with and without Mg(II).

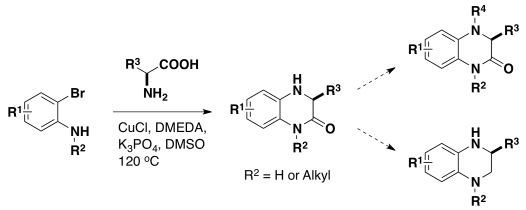
Figure II-4. Hits from thermal shift assays against GSK3β in the absence (red value) or presence (blue value) of Mg(II).



2. Initial SAR of several analogues and their inhibitory activities

Compounds **63-65** were synthesized via a tandem Ullmann reaction/cyclodehydration sequence[85] from different starting materials (Scheme **II-8**). Specifically, the sequence involves a one-pot reaction involving an intermolecular cross-coupling reaction between an amino group of the amino acid and an aryl bromide, followed by an intramolecular cyclization reaction that forms the amide bond. There are several desirable features of this reaction. First, aryl bromides with different substitutions can be used including the pyridyl bromide. Second, the other building block of this reaction is an amino acid. Various amino acids, either naturally occurring or non-naturally occurring, are commercially available with both enantiomers. Rapid access to analogues and stereoisomers will enable efficient growth of the fragment once a hit is identified, which also facilitates the study of (stereochemical) structure-activity relationships. Third, the free amine group can be easily modified, and the secondary amide moiety can be reduced to the corresponding amine. Last, starting with a secondary amine (R^2 = alkyl), the tertiary amide can be accessed that has totally different hydrogen bonding ability and sterics compared to the secondary amide.

Scheme II-8. Versatility of the Ullmann reaction/cyclodehydration sequence.

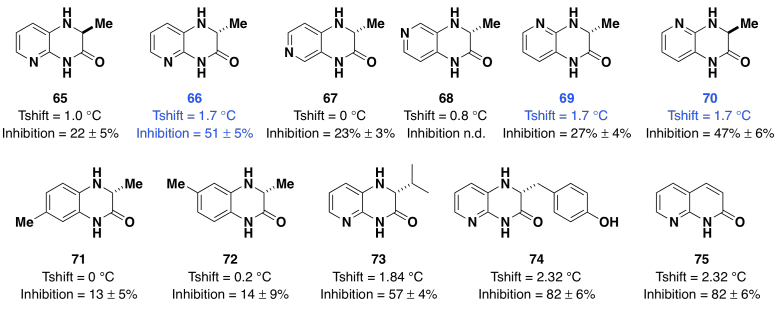


However, there are several notable problems associated with this reaction. First, the

reaction is performed at 120 °C. Under such harsh conditions, epimerization of the chiral center within the amino acid occurs potentially at any stage of the reaction. Second, the use of aryl-substituted glycines leads to serious decomposition without isolation of desired product. Third, certain products can be further oxidized to the imine in solution at room temperature, eliminating the chiral center and posing challenges for storage of such compounds in a stock solution. To overcome the third limitation, small aliquots of each compound (mostly crystalline powders) were prepared and stored at -20 °C. Before running the assays, each compound was made freshly and discarded at the end of the day.

Enabled by the efficient Ullmann reaction, analogues were easily accessed. Thermal shifts of these compounds were obtained and listed in Figure **II-5**. At this point, we were interested in whether these compounds will inhibit the kinase activity of GSK3β. An ADP-Glo^{TM} assay was adopted for this purpose. We measured the inhibitory activity of the compounds at a single concentration of 1 mM whenever soluble. The results are shown in Figure **II-5**.

Figure II-5. Results of thermal shift assay and inhibition assay with several analogues.



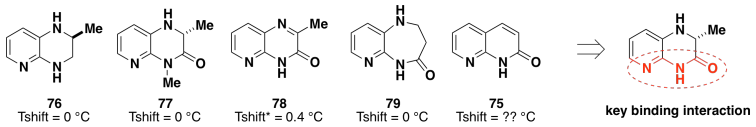
If the inhibitory activity is caused by non-specific aggregation of the compound, both enantiomers will have the same activity since enantiomers have the same physicochemical properties. Our results showed that the (*R*)-enantiomer **66** is more active than the (*S*)-enantiomer **65**, which suggests the binding interaction and inhibitory activity are real and not due to promiscuous interactions. Other results also showed that the position of the pyridyl nitrogen matters. Among the four regioisomers **66**-**69**, compound **66** with nitrogen atom adjacent to the amide yielded the optimal scaffold. Interestingly, when the pyridyl nitrogen is adjacent to the amine, the (*R*)-enantiomer **69** is less active than the (*S*)-enantiomer **70**. The reversion of stereochemical SAR indicated that the binding modes of the two scaffolds (**65**, **66** versus **69**, **70**) are probably different from each other.

3. Identification of the key binding motif of a particular scaffold

We chose to follow up with the enantiomeric pair **65** and **66** first. It has been reported that a pyridylamide moiety is able to form a hydrogen-bonding network with the backbone carbonyl and amide hydrogen of the peptide through the amide hydrogen and pyridyl nitrogen.[86-88] We hypothesized that this moiety is a key interaction for the small fragment. To test our hypothesis, perturbations of the moiety or the pattern were achieved synthetically (Figure **II-6**). The secondary amide of compound **65** was reduced to generate the secondary amine **76**, thereby deleting the carbonyl oxygen that previously served as a hydrogen bond accepter, and abolishing the binding interaction. Starting from N-methyl bromopyridylamine, tertiary amide **77** was obtained which not only removed the hydrogen bond donor ability but also increase the steric hindrance of the amide; and

again the binding interaction was abolished. A 7-membered analogue **79** was made to disturb the dihedral angle between the pyridyl group and the amide moiety, and it is also inactive compared to the parent compound. However, changes that have little interference with the key binding motif retain activity to some degree such as compound **75** (commercially available) and **78** (accessed via oxidation of **65**).

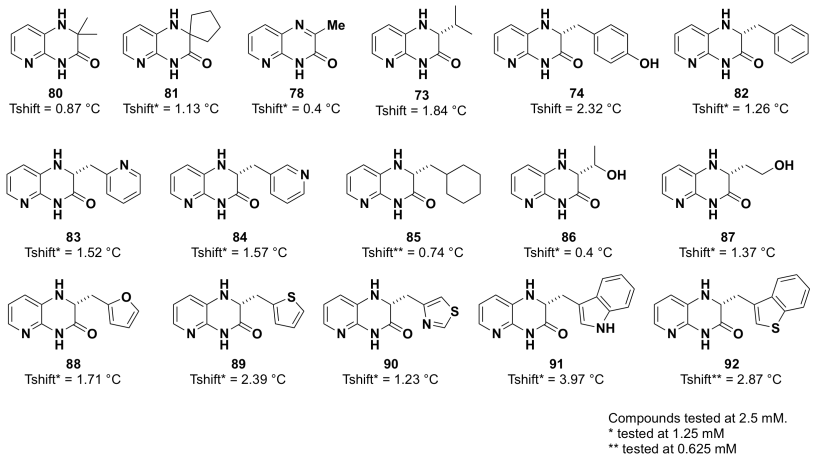
Figure II-6. Key binding interaction probed by perturbations of compound **65** and **66**.



4. Growth of the fragment to improve potency and confirmation by NMR and ITC

After the recognition of the key binding motif, we pursued the question of where to grow compound **66** to increase potency (Figure **II-7**). Increased potency of compound **73** and **74** indicated that there might be a pocket at the position where the substituent is pointing.

Figure II-7. Growth of fragment **66** to increase potency.

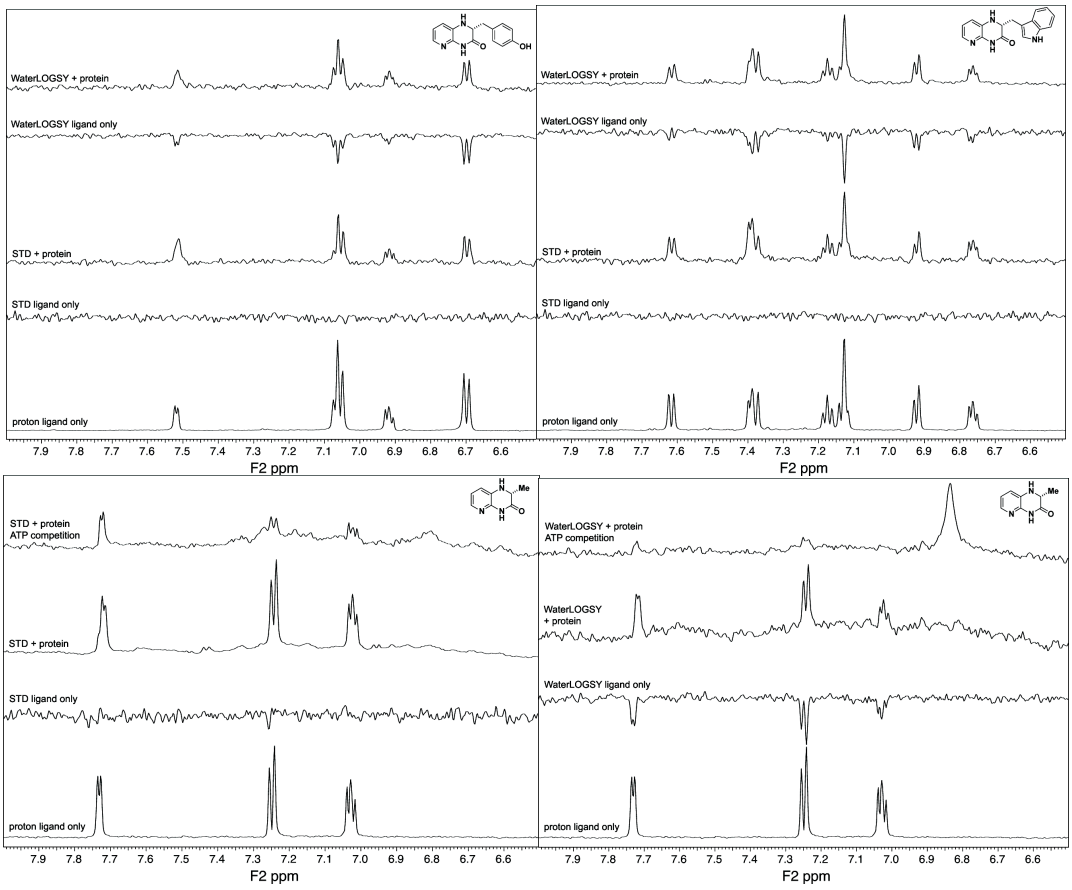


The geminal-dimethyl analogue **80** and cyclobutenyl analogue **81** were synthesized and shown to be less potent. The oxidized product **78** also displays less potency. Taken all together, these results indicated that the orientation of the substituent is important for picking up the favorable interactions, and there might be a hydrophobic pocket. Therefore, several analogues containing substituted alkyl, gem-dialkyl, benzyl, hydroxybenzyl, and heteroaromatic substituents from the corresponding amino acids were synthesized and tested using the thermal shift assay. Generally speaking, compounds that have heteroaromatic groups increase the binding interaction, among which the indole analogue **91** was found to be the most potent one.

STD and WaterLOGSY experiments[41,44] were performed to confirm the binding interaction between compounds **66**, **74**, and **91** with GSK3β. The results are shown in Figure **II-8**. Using 5 μM of GSK3β and 500 μM of compound **74** or **91** for the NMR experiment, binding interactions of both were clearly shown in either experiment indicated by the increase of ligand signal in the presence of GSK3β. For compound **66**, the binding interaction was also observed at 5 μM of GSK3β. However, the results shown in Figure **II-8** were performed with 20 μM of GSK3β and 500 μM ligand in order to increase the signal/noise ratio. Next, an ATP competition assay was performed to determine whether compound **66** is an ATP-competitive binder or not. When ATP was added to the solution with both protein and compound **66** at a final concentration of 500 μM in the presence of 10 mM $MgCl_2$, signals corresponding to ATP were observed, which can be more clearly seen in the WaterLOGSY experiment. Interestingly, decreases of ligand signals in both experiments were observed indicating that ATP was competing

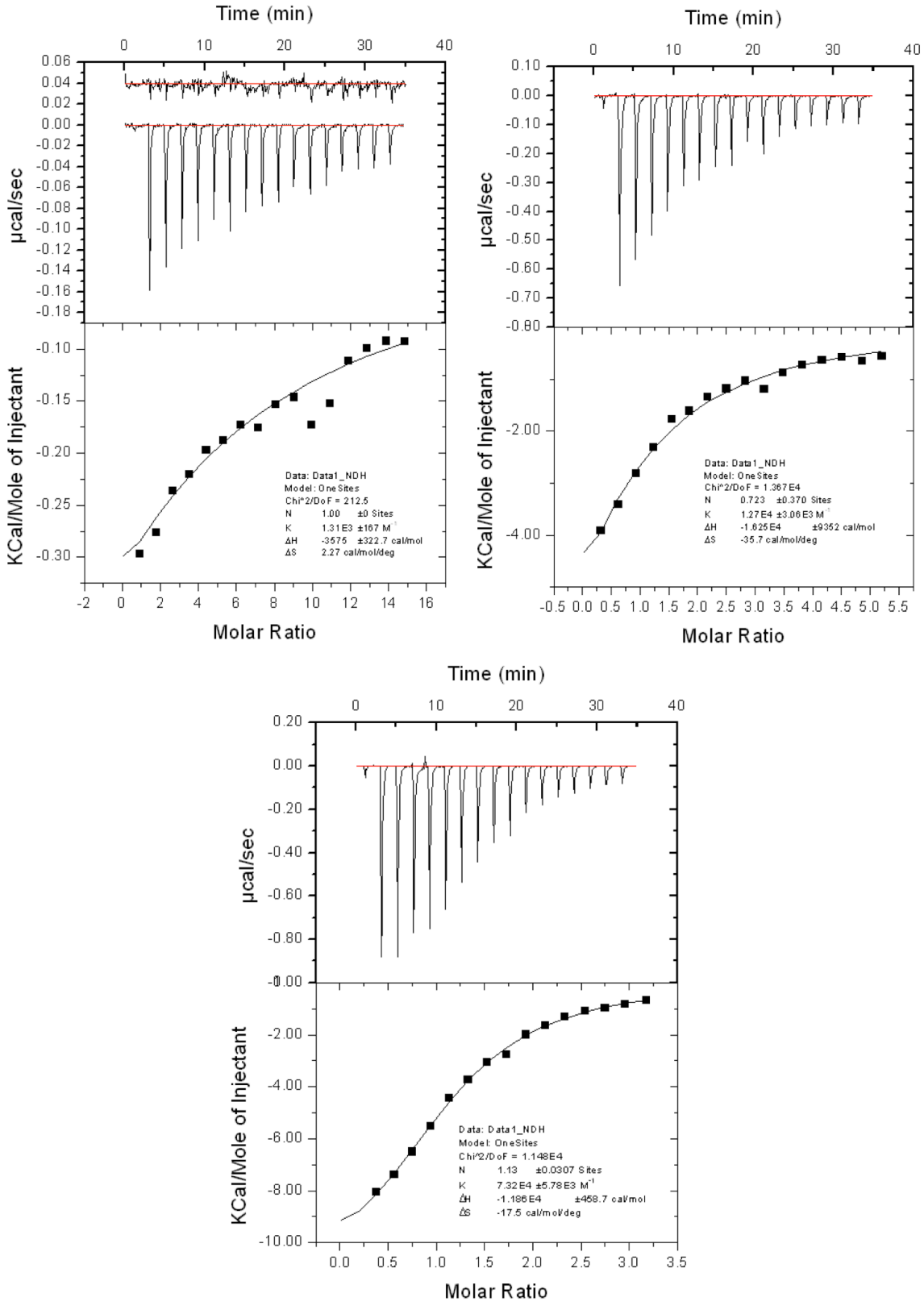
with compound **66**.

Figure II-8. STD and WaterLOGSY NMR experiment of compound **74** (top left), **91** (top right), and **66** (bottom two).



ITC experiments were then performed to measure the binding constant of compounds **66**, **74**, and **91** (Figure **II-9**). The K_d of each compound was determined to be 0.9 mM, 80 μM, 14 μM respectively, which correlate well with their thermal shift values.

Figure II-9. ITC results of compound **66** (top left), **74** (top right), and **91** (bottom).



5. Current exploration and future directions

X-Ray crystallography studies are being performed in Prof. Steve Almo's group, which will help us to capture the binding interactions and guide further optimization of the inhibitor in a rational way.

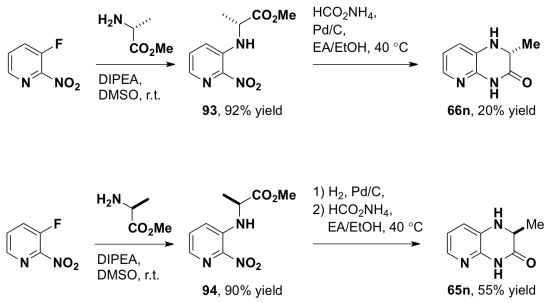
Until all the experiments mentioned above were completed, the enantiopurity of some compounds was measured by chiral SFC analysis. The enantiomeric excess (*ee*) of compound **66** is 62%, of **67** is 98%, of **68** is 98%, of **69** is 80%, of **70** is 28%, of **91** is 34%. These results indicate that the racemization of the chiral center during the Ullmann reaction is a serious problem. Without enantiomerically pure forms of these compounds, the comparison between them is invalid, and K_d or IC_{50} values of the grown fragments are not accurate.

We explored ways to make the enantiopure compounds either by recrystallization or via a different synthetic route for compounds that cannot be easily recrystallized. It was found that the *ee* of compound **66** was improved by about 5-10% after one round of recrystallization from an initial *ee* of around 50%. At the same time, a different synthetic route was explored according to a reported procedure.[89] As shown in Scheme **II-9**, 3-fluoro-2-nitropyridine underwent a S_NAr reaction with an amino ester to generate compound **93**. The one-pot reduction/cyclization under transfer-hydrogenation conditions was low yielding. Nevertheless, the *ee* of isolated product **66n** is determined to be 98%. To improve yield of this reaction, classical hydrogenation condition with H_2 and Pd/C was adopted. The reduction of the nitro group in compound **94** was finished after 3 hours.

However, the cyclization did not proceed efficiently. Ammonium formate was then added to the reaction mixture after removal of H_2 from the flask. The reaction went to completion after 12 hours at 40 °C, yielding the desired product **65n** with 55% yield and 98% *ee*. This new route did lead to a remarkable improvement of enantiopurity compared to the Ullmann reaction. Patrick Sheehan is currently resynthesizing several key compounds with high enantiopurity so that a valid comparison can be made and accurate binding affinities can be determined.

Another way of solving the enantiopurity issue is to run the Ullmann reaction with α-disubstituted amino acids. By having a α-methyl group instead of the α-H in compound **91**, both the epimerization and oxidation can be prevented at the same time.

Scheme II-9. Synthetic route towards enantiopure aza-quinoxalinone.



Chapter II-4. Conclusion and Future Directions

The concept of DOS was applied to the synthesis of novel fragment libraries to expand into the chemical space not covered by traditional fragments. The DOS fragment library was designed to have higher sp^3 content and more stereochemical and skeletal diversity compared to commercial fragment libraries. Modular synthetic pathways following the logic of B/C/P has enabled the access of all possible stereoisomers in their enantiopure forms. The inclusion of all stereoisomers provided primary SSAR information that was used to distinguish between specific binders from nonspecific binders and guide modification of the initial hit. Synthetic accessibility of derivatives of building blocks and pre-imbedded versatile functional groups allowed rapid access of analogues to gain SAR information and optimization of the initial hit. Such efforts can be made to increase the potency of the initial hit prior to the gathering of structural information from X-Ray crystallography studies.

To evaluate the DOS fragments that have been synthesized, GSK3β was selected as the proof-of-concept target. After initial hits were identified by thermal shift screenings, analogues were made efficiently via the Ullmann reaction and evaluated by thermal shift assays and biochemical assays. The K_D was rapidly improved from 0.9 mM to 14 μM as determined by ITC experiments. However, the enantiopurity of analogues accessed by the Ullmann reaction are not consistently high, which complicated the comparison between different analogues and the determination of binding affinities of these compounds. The experience so far taught us that the design of synthetic pathways and the quality of the compounds within a library are very important for the success and

efficiency of the fragment-based approach and are worth the proactive effort. Progress is currently being made to solve the enantiopurity issue of the analogues. In addition, various DOS fragments from different synthetic pathways including the ones mentioned before are being made to increase the size of our library. These novel libraries will be screened against a broad array of biological targets to evaluate their biological activities.

Experimental Section

1. Material and Methods

Except as otherwise noted, reactions were carried out under argon. All reaction solvents except acetone and pyridine were dispensed from a solvent purification system wherein solvents are passed through a packed activated alumina column. Acetone was Aldrich 99.5+% histological grade. Pyridine was Aldrich 99.8% histological grade. NMR spectra were recorded at 500 MHz or 300 MHz using a Varian I-500 or M-300 instrument. Chemical shifts for proton NMR spectra are reported in parts per million downfield from tetramethylsilane and were referenced to residual protonated solvent ($CHCl_3$: d 7.26, C_6H_6: d 7.15, CH_3OH: 3.34, DMSO: 2.54). Chemical shifts for carbon NMR spectra are reported in parts per million downfield from tetramethylsilane and referenced to protonated solvent ($CHCl_3$: d 77.0, C_6H_6: d 128.0, CH_3OH: 49.9, DMSO: 39.5). Data are represented as follows: chemical shift (multiplicity [bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet], coupling constants in Hertz, integration). High-resolution mass spectra were obtained through the Harvard University mass spectrometry facility. Infrared spectra were obtained with a Nicolet IR100 FTIR from Thermo Scientific. Optical rotations were obtained using digital polarimeter Autopol IV (Rudolph research Analytical) with a 1 mL cell and a 1 dm path length. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 precoated plates (0.25 mm). Flash chromatography was performed either with the indicated solvent on E. Merck silica gel 60 (230-400 mesh) or using a CombiFlash companion system (Teledyne ISCO, Inc.) with pre-packed FLASH silica gel columns (Teledyne ISCO, Inc.). SFC/MS chromatography was performed with

a Berger analytic SFC (Waters ZQ Mass Spectometer) using CO_2 and isopropanol as the mobile phase and using a Chiralpak® AD-H column purchased from Chiral Technology Inc. (column length: 4.6x250mm, particle size: 5um).

2. Experimental procedures

A. Synthesis of proline-based fragment library

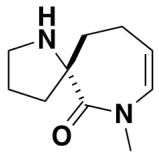
The syntheses and characterizations of compounds **1-34** can be found in the paper (*Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 6799). The synthetic procedures of compounds **35-44** (Scheme **II-4**) are described as followings.

To a stirred solution of proline derivative **3'** (0.200 g, 0.78 mmol), allyamine (0.067 g, 1.18 mmol), ethyl(hydroxyimino)cyanoacetate (0.167 g, 1.18 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.225 g, 1.18 mmol) in dichloromethane (16 mL) was added triethylamine (0.328 mL, 2.35 mmol). The reaction was stirred for 4 h at 23 °C. Saturated aqueous sodium bicarbonate (15 mL) was added to the reaction mixture and the aqueous phase was extracted with dichloromethane (3 x 15 mL). The combined extracts were dried over sodium sulfate and concentrated *in vacuo*. Purification by column chromatography (gradient 20 – 30% ethyl acetate/hexane) gave the ally amide **35** as colourless oil (0.210 g, 91%).

To a stirred solution of ally amide **35** (0.066 g, 0.22 mmol) in anhydrous dimethylformamide (4.5 mL), methyl iodide (0.64 g, 4.5 mmol) was added. The resulting solution was cooled to 0 °C and sodium hydride (60% in mineral oil, 26.9 mg,

0.67 mmol) was added. The reaction was stirred for 4 h at 0 °C. Saturated aqueous ammonium chloride (20 mL) was added to the reaction mixture and the aqueous phase was extracted with dichloromethane (3 x 15 mL). The combined extracts were dried over sodium sulfate and concentrated *in vacuo*. Purification by column chromatography (gradient 20 – 30% ethyl acetate/hexane) gave **36** as colourless oil (0.050 g, 72%).

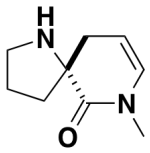
To a stirred mixture of **36** (0.070 g, 0.23 mmol) in anhydrous toluene (23 mL) was added Grubbs 2nd generation catalyst (0.019 g, 0.02 mmol). The reaction mixture was heated to 50 °C for 4 h followed by the addition of another portion of Grubbs 2nd generation catalyst (0.019 g, 0.02 mmol). After another 12 hours at 50 °C, ethylvinylether (0.327 g, 4.5 mmol) was added to the reaction and then the solvent was removed *in vacuo*. Purification by column chromatography (gradient 25 – 60% ethyl acetate/hexane) gave product **37** as yellow oil (0.038 g, 60%) and product **38** (0.005 g, 8%) as yellow oil. Deprotection of the Boc group on either product was performed in 2 ml neat trifluoroacetic acid for 5 minutes. The reaction was then concentrated *in vacuo*. The remaining TFA was quenched with anhydrous Na_2CO_3. The extracts were extracted with DCM and concentrated *in vacuo* respectively to give product **39** and **40** (quantitative).



(*S*)-7-methyl-1,7-diazaspiro[4.6]undec-8-en-6-one (39)

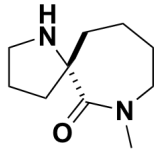
^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.86 (d, *J* = 9.5 Hz, 1 H), 5.36 (ddd, *J* = 9.5, 4.5, 4.5 Hz, 1 H), 3.65-3.60 (m, 1 H), 3.42-3.37 (m, 1 H), 3.17 (s, 3 H), 2.65-2.61 (m, 1 H), 2.51-2.46

(m, 1 H), 2.40-2.22 (m, 4H), 2.19-2.14 (m, 1 H), 1.87-1.79 (m, 1 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 170.8, 128.4, 117.1, 73.0, 45.5, 37.9, 31.9, 31.9, 23.8, 23.6; HRMS (ESI-TOF) calcd. for $C_{10}H_{16}N_2O$ $[M+H]^+$ 181.13354, found 181.13419.



(*R*)-7-methyl-1,7-diazaspiro[4.5]dec-8-en-6-one (40)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.00-5.98 (m, 1 H), 5.16-5.12 (m, 1 H), 3.25-3.21 (m, 1 H), 3.09 (s, 3 H), 3.08-3.04 (m, 1 H), 2.53-2.49 (m, 1 H), 2.33 (dd, *J* = 17.0, 6.0 Hz, 1 H), 1.93-1.80 (m, 4 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 167.6, 130.5, 104.7, 66.9, 46.8, 35.0, 34.5, 29.7, 23.3; HRMS (ESI-TOF) calcd. for $C_9H_{14}N_2O$ $[M+Na]^+$ 189.09983, found 189.09997.



(*S*)-7-methyl-1,7-diazaspiro[4.6]undecan-6-one (22)

A solution of **39** (0.007 g, 0.039 mmol) and palladium hydroxide (20 wt.% Pd on carbon, wet, 0.011 g) in methanol (8 mL) was stirred at 25 ^{o}C under an atmosphere of hydrogen gas for 16 h. The suspension was then filtered through a Celite pad and the filtrate was concentrated *in vacuo* to give compound **22** as a yellow solid (0.006 g, 90%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.46 (bs, 1H), 3.60-3.54 (m, 2H), 3.36-3.31 (m, 1H), 3.29-3.25 (m, 1H), 3.08 (s, 3H), 2.35-2.30 (m, 2H), 2.25-2.15 (m, 2H), 2.03-1.85 (m, 4H), 1.72-1.63

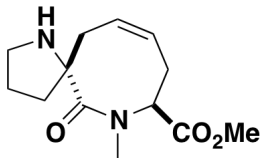
(m, 1H), 1.53-1.45 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 171.7, 73.4, 51.1, 45.1, 39.0, 32.0, 31.8, 26.9, 25.0, 24.6; HRMS (ESI-TOF) calcd. for $C_{10}H_{18}N_2O$ $[M+H]^+$ 183.14919, found 183.14985.

To a stirred solution of proline derivative **3'** (0.110 g, 0.43 mmol), (*S*)-methyl 2-aminopent-4-enoate trifluoroacetic acid (0.125 g, 0.52 mmol), ethyl(hydroxyimino)cyanoacetate (0.092 g, 0.65 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.124 g, 0.65 mmol) in dichloromethane (16 mL) was added triethylamine (0.240 mL, 1.72 mmol). The reaction was stirred for 4 h at 25 °C. Saturated aqueous sodium bicarbonate (15 mL) was added to the reaction mixture and the aqueous phase was extracted with dichloromethane (15 mL, 3 times). The combined extracts were dried over sodium sulfate and concentrated *in vacuo*. Purification by column chromatography (gradient 20 – 30% ethyl acetate/hexane) gave the ally amide **41** as colourless oil (0.140 g, 89%).

To a stirred solution of the secondary amide **41** (0.140 g, 0.38 mmol) in anhydrous dimethylformamide (7.6 mL), methyl iodide (2.17 g, 15.3 mmol) was added. The resulting solution was cooled to 0 °C and sodium hydride (60% in mineral oil, 45.8 mg, 1.15 mmol) was added. The reaction was stirred for 4 h at 0 °C. Saturated aqueous ammonium chloride (20 mL) was added to the reaction mixture and the aqueous phase was extracted with dichloromethane (15 mL, 3 times). The combined extracts were dried over sodium sulfate and concentrated *in vacuo*. Purification by column chromatography

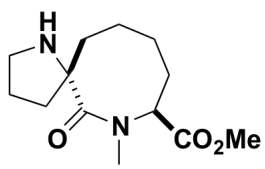
(gradient 20 – 30% ethyl acetate/hexane) gave the tertiary amide **42** as colourless oil (0.129 g, 89%).

To a stirred mixture of **42** (0.129 g, 0.34 mmol) in anhydrous dichloromethane (16 mL) was added Grubbs 2nd generation catalyst (0.058 g, 0.07 mmol). The reaction mixture was heated to reflux for 16 h. The solvent was removed *in vacuo*. Purification by column chromatography (gradient 25 – 45% ethyl acetate/hexane) gave product **43** as a white solid (0.012 g, 34%). Deprotection of the Boc group on either product with 2 ml neat trifluoroacetic acid followed by concentration *in vacuo* gave the product **44** as yellow oil (quantitative).



(5*R*,8*S*,*Z*)-methyl 7-methyl-6-oxo-1,7-diazaspiro[4.7]dodec-10-ene-8-carboxylate (44)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.75-5.68 (m, 2 H), 5.20 (dd, *J* = 10.2, 6.2 Hz, 1 H), 3.78 (s, 3 H), 3.49 (bs, 2 H), 3.17-3.13 (m, 1 H), 2.87-2.83 (m, 5 H), 2.78-2.71 (m, 1 H), 2.51-2.47 (m, 1 H), 2.17-2.08 (m, 2 H), 2.03-1.98 (m, 1 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 169.7, 168.9, 129.8, 125.1, 73.0, 59.6, 52.9, 45.8, 36.9, 35.0, 33.9, 28.0, 22.4; HRMS (ESI-TOF) calcd. for $C_{13}H_{20}N_2O_3$ $[M+H]^+$ 253.15467, found 253.15519.

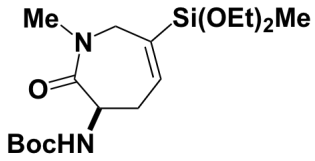


(5*S*,8*S*)-methyl 7-methyl-6-oxo-1,7-diazaspiro[4.7]dodecane-8-carboxylate (27)

A solution of **44** (0.019 g, 0.075 mmol) and palladium hydroxide (20 wt.% Pd on carbon, wet, 0.011 g) in methanol (8 mL) was stirred at 25 °C under an atmosphere of hydrogen gas for 2 h. The suspension was then filtered through a Celite pad and the filtrate was concentrated *in vacuo* to give compound **27** as yellow oil (0.016 g, 84%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.80 (dd, *J* = 7.5, 7.5 Hz, 1 H), 3.80 (s, 3 H), 3.50-3.43 (m, 2 H), 2.95 (s, 3 H), 2.63-2.60 (m, 1 H), 2.26-2.16 (m, 2 H), 2.11-2.01 (m, 4 H), 1.98-1.92 (m, 1 H), 1.83-1.79 (m, 1 H), 1.70-1.61 (m, 2 H), 1.36-1.28 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.7, 171.8, 74.7, 61.6, 53.3, 47.8, 39.5, 36.8, 28.6, 23.5, 23.4, 22.5; HRMS (ESI-TOF) calcd. for $C_{13}H_{22}N_2O_3$ $[M+H]^+$ 255.17032, found 255.17059.

B. Synthesis of alkenylsiloxane-based fragment library

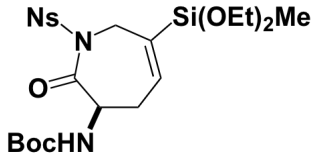
Following the general hydrosilylation and RCM procedures described in Chapter **I-7-2**, compounds **46**, **51**, and **53** were efficiently synthesized.



(*R*)-*tert*-butyl (6-(diethoxy(methyl)silyl)-1-methyl-2-oxo-2,3,4,7-tetrahydro-1*H*-azepin-3-yl)carbamate (46)

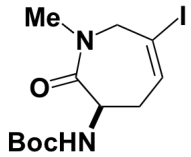
Yield 62% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.18-6.17 (m, 1 H), 5.79 (d, *J* = 5.5 Hz, 1 H), 4.99-4.94 (m, 1 H), 4.43-4.39 (m, 1 H), 3.78-3.69 (m, 4 H), 3.52 (d, *J* = 17.5 Hz, 1 H), 3.01 (s, 3 H), 2.79-2.73 (m, 1 H), 2.26-2.20 (m, 1 H), 1.42 (s, 9 H), 1.19 (t,

J = 7.0 Hz, 6 H), 0.15 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.0, 155.1, 142.2, 133.3, 79.5, 58.4, 49.2, 48.0, 35.7, 35.2, 28.3, 18.2, -5.5.



(*R*)-*tert*-butyl (6-(diethoxy(methyl)silyl)-1-((2-nitrophenyl)sulfonyl)-2-oxo-2,3,4,7-tetrahydro-1*H*-azepin-3-yl)carbamate (51)

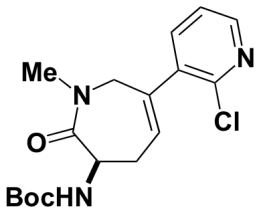
Yield 70% (colorless oil); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.46-8.44 (m, 1 H), 7.80-7.75 (m, 3 H), 6.32 (dd, *J* = 2.7, 2.7 Hz, 1 H), 5.40 (d, *J* = 7.0 Hz, 1 H), 5.10-5.06 (m, 1 H), 4.86 (d, *J* = 17.0 Hz, 1 H), 4.51-4.47 (m, 1 H), 3.82-3.75 (m, 1 H), 2.88-2.84 (m, 1 H), 2.48-2.42 (m, 1 H), 1.38 (s, 9 H), 1.27-1.22 (m, 6 H), 0.26 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.5, 154.5, 147.9, 141.7, 134.7, 134.7, 1333.3, 132.9, 132.0, 124.6, 81.1, 58.6, 58.6, 51.1, 44.2, 35.4, 28.2, 18.2, -5.0.



(*R*)-*tert*-butyl (6-iodo-1-methyl-2-oxo-2,3,4,7-tetrahydro-1*H*-azepin-3-yl)carbamate (48)

To a stirred solution of compound **46** (155 mg, 0.42 mmol) in HFIP (6 mL) was added NIS (281 mg, 1.25 mmol) at room temperature. The resulting mixture was warmed up to 50 °C, and stirred for 3 hours. The reaction was then quenched with aqueous $Na_2S_2O_3$ (10 %), extracted with EA. The extract was concentrated *in vacuo* and purified by column

chromatography (gradient 10 – 40% ethyl acetate/hexane) to give compound **48** as yellowish oil (0.060 g, 61%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.38-6.35 (m, 1 H), 5.73 (d, *J* = 5.7 Hz, 1 H), 4.90-4.72 (m, 2 H), 3.71 (d, *J* = 18.6 Hz, 1 H), 3.08 (s, 3 H), 2.64-2.54 (m, 1H), 2.25-2.19 (m, 1 H), 1.39 (s, 9 H).



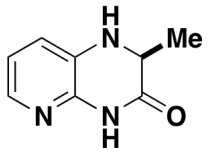
(*R*)-*tert*-butyl (6-(2-chloropyridin-3-yl)-1-methyl-2-oxo-2,3,4,7-tetrahydro-1*H*-azepin-3-yl) carbamate (49)

Following the procedure described in ref. 80, to a stirred solution of compound **48** (80 mg, 0.22 mmol) in DMF (8 mL) was added (2-chloropyridin-3-yl)boronic acid (52 mg, 0.33 mmol), DPPF (8.5 mg, 15 μmol), and sodium carbonate solution (0.65 mL, 1 M). The resulting mixture was warmed up to 70 °C and stirred for 3 hours. The reaction was then cooled to room temperature after 2 hours, quenched with water, extracted with EA (3 times). The extract was washed with brine, dried with sodium sulfate, concentrated *in vacuo* and purified by column chromatography (25-55% EA in hexane) to afford the title compound as yellowish solid (65 mg, 63%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.31-8.29 (m, 1 H), 7.48-7.45 (m, 1 H), 7.23-7.19 (m, 1 H), 5.87 (d, *J* = 6.3 Hz, 1 H), 5.73-5.71 (m, 1 H), 5.07-4.99 (m, 1 H), 4.87-4.78 (m, 1 H), 3.52 (d, *J* = 17.4 Hz, 1 H), 3.11 (s, 3 H), 2.88-2.78 (m, 1 H), 2.39-2.27 (m, 1 H), 1.42 (s, 9 H).

C. Synthesis of GSK3β inhibitors

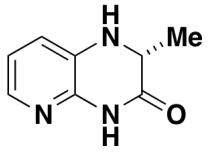
The syntheses and characterizations of compounds **60** and **61** can be found in the paper (*Org. Lett.* **2011**, *13*, 5556).

General procedure for Ullmann reaction/cyclodehydration sequence: adapted from the reported procedure, in a pressure tube, a suspension of 2-bromoaniline (1 equiv.), amino acid (2 equiv.), K_3PO_4 (2 equiv.), cuprous (I) chloride (2 mol%), and *N*,*N*′-dimethylethylenediamine (DMEDA) (20 mol%) in dry DMSO (0.3 M) was deoxygenated with argon and sealed with PTFE plug. The reaction mixture was then stirred at 120°C for 24 h. The mixture was treated with water (20 mL) and the mixture was extracted three times with EtOAc. The combined organic layers were dried over anhydrous sodium sulfate. After filtration, solvent was evaporated to give the crude product, which was subjected to chromatography on silica gel (hexanes/EtOAc or DCM/MeOH) providind the desired compound.



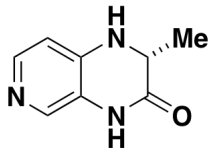
(*S*)-2-methyl-1,2-dihydropyrido[2,3-*b*]pyrazin-3(4*H*)-one (65)

Yield 24% (yellowish solid); ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.7 (s, 1 H), 7.61-7.59 (m, 1 H), 7.01-7.00 (m, 1 H), 6.84-6.81 (m, 1 H), 6.28 (s, 1 H), 3.92-3.88 (m, 1 H), 1.30 (d, *J* = 7.0 Hz, 3 H); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 169.1, 140.7, 136.1, 130.2, 118.9, 118.6, 50.7, 17.7.



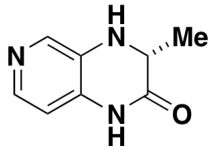
(*R*)-2-methyl-1,2-dihydropyrido[2,3-*b*]pyrazin-3(4*H*)-one (66)

Yield 46% (yellowish solid); ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.7 (s, 1 H), 7.61-7.59 (m, 1 H), 7.01-7.00 (m, 1 H), 6.84-6.81 (m, 1 H), 6.28 (s, 1 H), 3.92-3.88 (m, 1 H), 1.30 (d, *J* = 7.0 Hz, 3 H); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 169.1, 140.7, 136.1, 130.2, 118.9, 118.6, 50.7, 17.7.



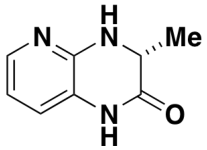
(*R*)-2-methyl-1,2-dihydropyrido[3,4-*b*]pyrazin-3(4*H*)-one (67)

Yield 6% (brown solid); ^{1}H-NMR (500 MHz, CD_3OD) δ 7.79 (d, *J* = 5.5 Hz, 1 H), 7.75 (s, 1 H), 6.63(d, *J* = 5.5 Hz, 1 H), 4.59 (s, 2 H), 4.10 (q, *J* = 7.0 Hz, 1 H), 1.40 (d, *J* = 7.0 Hz, 3 H).



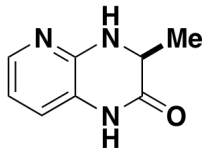
(*R*)-3-methyl-3,4-dihydropyrido[3,4-*b*]pyrazin-2(1*H*)-one (68)

Yield 14% (brown solid); ^{1}H-NMR (500 MHz, CD_3OD) δ 7.88 (s, 1 H), 7.79 (d, *J* = 4.0 Hz, 1 H), 6.76 (d, *J* = 5.0 Hz, 1 H), 3.97 (q, *J* = 6.5 Hz, 1 H), 3.34 (s, 1 H), 1.38 (d, *J* = 6.0 Hz, 3 H); ^{13}C-NMR (125 MHz, CD_3OD) δ 168.7, 139.7, 134.6, 132.4, 130.9, 109.1, 50.7, 17.5.



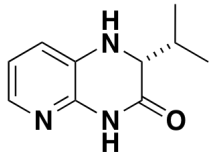
(*R*)-3-methyl-3,4-dihydropyrido[2,3-*b*]pyrazin-2(1*H*)-one (69)

Yield 33% (yellowish solid); ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.4 (s, 1 H), 7.66-7.65 (m, 1 H), 6.97-6.96 (m, 1 H), 6.85 (s, 1 H), 6.62-6.59 (m, 1 H), 4.05-4.01 (m, 1 H), 1.33 (d, *J* = 7.0 Hz, 2 H).



(*S*)-3-methyl-3,4-dihydropyrido[2,3-*b*]pyrazin-2(1*H*)-one (70)

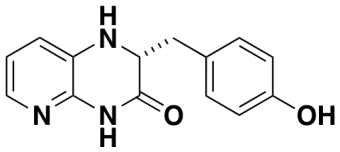
Yield 18% (yellowish solid); ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.4 (s, 1 H), 7.66-7.65 (m, 1 H), 6.97-6.96 (m, 1 H), 6.85 (s, 1 H), 6.62-6.59 (m, 1 H), 4.05-4.01 (m, 1 H), 1.33 (d, *J* = 7.0 Hz, 2 H); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 167.5, 147.0, 141.0, 120.8, 119.9, 113.3, 50.8, 18.5.



(*R*)-2-isopropyl-1,2-dihydropyrido[2,3-*b*]pyrazin-3(4*H*)-one (73)

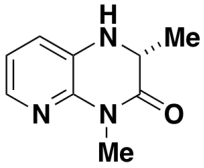
Yellowish solid; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.56 (d, *J* = 5.0 Hz, 1 H), 7.02 (d, *J* = 7.5 Hz, 1 H), 6.81 (dd, *J* = 7.0, 5.0 Hz, 1 H), 3.76 (d, *J* = 5.0 Hz, 1 H), 2.13-2.07 (m, 1

H), 1.00 (d, *J* = 7.0 Hz, 3 H), 0.92 (d, *J* = 7.0 Hz, 3 H); ^{13}C-NMR (125 MHz, CD_3OD) δ 170.5, 140.6, 136.6, 131.8, 120.6, 120.1, 62.8, 33.4, 19.1, 17.8.



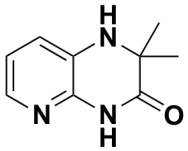
(*R*)-2-(4-hydroxybenzyl)-1,2-dihydropyrido[2,3-*b*]pyrazin-3(4*H*)-one (74)

Yellowish solid; ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.6 (s, 1 H), 9.15 (s, 1 H), 7.47-7.46 (m, 1 H), 6.95-6.93 (m, 3 H), 6.74-6.72 (m, 1 H), 6.61 (d, *J* = 8.0 Hz, 2 H), 6.04 (s, 1 H), 4.04-4.01 (m, 1 H), 2.82 (dd, *J* = 13.5, 4.5 Hz, 1 H), 2.75 (dd, *J* = 13.5, 7.0 Hz, 1 H); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 167.8, 155.8, 139.9, 135.5, 130.6, 129.5, 126.8, 118.7, 118.6, 56.9, 37.4.



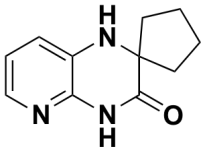
(*R*)-2,4-dimethyl-1,2-dihydropyrido[2,3-*b*]pyrazin-3(4*H*)-one (77)

Yield 79% (yellowish solid); ^{1}H-NMR (500 MHz, d_6-DMSO) δ 7.75-7.74 (m, 1 H), 7.08-7.06 (m, 1 H), 6.92-6.89 (m, 1 H), 6.38 (s, 1 H), 3.98 (q, *J* = 6.5 Hz, 1 H), 3.35 (s, 3 H), 1.32 (d, *J* = 7.0 Hz, 3 H).



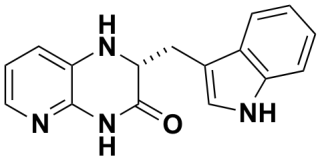
2,2-Dimethyl-1,2-dihydropyrido[2,3-*b*]pyrazin-3(4*H*)-one (80)

Yellowish solid; ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.6 (s, 1 H), 7.62-7.61 (m, 1 H), 7.01-7.00 (m, 1 H), 6.85-6.82 (m, 1 H), 6.25 (s, 1 H), 1.27 (s, 6 H).



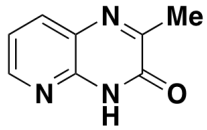
1'*H*-spiro[cyclopentane-1,2'-pyrido[2,3-*b*]pyrazin]-3'(4'*H*)-one (81)

Yellowish solid; ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.6 (s, 1 H), 7.62-7.61 (m, 1 H), 7.05-7.03 (m, 1 H), 6.84-6.82 (m, 1 H), 6.34 (s, 1 H), 2.08-2.03 (m, 2 H), 1.82-1.75 (m, 2 H), 1.70-1.56 (m, 4 H).



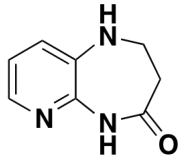
(*R*)-2-((1*H*-indol-3-yl)methyl)-1,2-dihydropyrido[2,3-*b*]pyrazin-3(4*H*)-one (91)

Yellowish solid; ^{1}H-NMR (500 MHz, d_6-DMSO) δ 10.8 (s, 1 H), 10.6 (s, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 7.47-7.46 (m, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 7.10-7.09 (m, 1 H), 7.04 (dd, *J* = 7.0, 7.0 Hz, 1 H), 6.96-6.91 (m, 2 H), 6.71 (dd, *J* = 7.5, 5.0 Hz, 1 H), 6.05-6.04 (m, 1 H), 4.15-4.12 (m, 1 H), 3.09 (dd, *J* = 15.0, 4.0 Hz, 1 H), 2.98 (dd, *J* = 15.0, 7.5 Hz, 1 H); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 168.2, 140.0, 136.1, 135.5, 129.5, 127.5, 124.1, 120.8, 118.7, 118.6, 118.3, 118.3, 111.3, 109.1, 56.2, 28.3.



2-Methylpyrido[2,3-*b*]pyrazin-3(4*H*)-one (78)

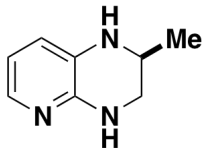
To a solution of 8% aqueous sodium hydroxide (1.0 mL) was added compound **65** (48 mg, 0.3 mmol) followed by a solution of 30 wt% hydrogen peroxide in water (0.6 mL). The reaction mixture was slowly heated to 80 °C and maintained at this temperature for 4 h. The heating source was removed, and acetic acid (0.5 mL) was added dropwise. The suspension was stirred overnight at room temperature and the precipitated solid was collected by filtration to afford the desired product **78** as white solid. ^{1}H-NMR (500 MHz, d_6-DMSO) δ 12.7 (bs, 1 H), 8.46 (s, 1 H), 8.10 (d, J = 7.5 Hz, 1 H), 7.33-7.31 (m, 1 H), 2.40 (s, 3 H); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 160.7, 156.2, 149.1, 144.0, 135.8, 126.8, 119.5, 20.5.



2,3-Dihydro-1*H*-pyrido[2,3-*b*][1,4]diazepin-4(5*H*)-one (79)

A pressure tube was charged with CuI (19 mg, 0.1 mmol), 2-bromoaniline (0.35 g, 2 mmol), 2-azetidinone (0.17 g, 2.4 mmol), and K_2CO_3 (0.86 g, 4.1 mmol), evacuated, and backfilled with argon. *N*,*N*′-Dimethylethylenediamine (DMEDA) (18 mg, 0.10 mmol) and DMF (10 mL) were added under argon. The pressure tube was sealed with a PTFE plug and the reaction mixture was stirred at 110 °C for 24 h in a preheated oil bath. The resulting brown-black suspension was allowed to reach room temperature, filtered

through a silica gel plug eluting with 10:1 CH_2Cl_2/MeOH (50 mL), and the red filtrate was concentrated. The oily residue was transferred to a pressure tube, which was then evacuated, backfilled with argon, and sealed with a rubber septum. $Ti(OiPr)_4$ (0.2 g, 0.7 mmol) and toluene (6 mL) was added to the pressure tube and the septum was replaced with a PTFE plug under a stream of argon. The sealed pressure tube was placed in an oil bath preheated to 120 °C. After being stirred at 120 °C for 24 h, the reaction mixture was allowed to reach room temperature and then filtered through a silica gel plug eluting with 10:1 CH_2Cl_2/MeOH (50 mL). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH) to provide the desired product as yellowish solid. ^{1}H-NMR (500 MHz, d_6-DMSO) δ 9.49 (s, 1 H), 7.66-7.53 (m, 1 H), 7.09 (d, J = 8.0 Hz, 1 H), 6.88-6.86 (m, 1 H), 5.98 (s, 1 H), 3.40 (dt, J = 5.0, 5.0 Hz, 2 H), 2.56 (t, J = 5.0 Hz, 2 H); ^{13}C-NMR (125 MHz, d_6-DMSO) δ 172.1, 138.8, 136.6, 135.2, 125.3, 119.7, 42.6, 37.5.



(*S*)-2-methyl-1,2,3,4-tetrahydropyrido[2,3-*b*]pyrazine (76)

To a stirred solution of compound **65** (22 mg, 0.14 mmol) in THF (1 mL) was added BH_3·THF solution (1 M, 0.67 mL) dropwise. The reaction was monitored by TLC until the disappearance of starting materials and then quenched with $NaHCO_3$ solution (saturated), extracted with EA (3 times). The extract was washed with brine, dried with sodium sulfate, concentrated *in vacuo* and purified by column chromatography (MeOH/DCM) to afford **76** as brown oil (10 mg, 48% yield). ^{1}H-NMR (500 MHz,

$CDCl_3$) δ 7.47 (d, *J* = 5.0 Hz, 1 H), 6.63 (d, *J* = 7.5 Hz, 1 H), 6.46 (dd, *J* = 7.5, 5.0 Hz, 1 H), 4.87 (bs, 1 H), 3.52-3.49 (m, 1 H), 3.43 (dd, *J* = 11.0, 2.5 Hz, 1 H), 3.17 (dd, *J* = 10.5, 8.5 Hz, 1 H), 1.20 (d, *J* = 6.5 Hz, 3 H).

D. Revised synthetic route

Adapted from ref. 89.

General procedure for S_NAr: to a stirred solution of 2-Nitro-3-fluoropyridine (1 equiv.) and methyl amino ester (or its hydrochloride salt, 2 equiv.) in DMSO (0.5 M) was added DIPEA (4 equiv.) at room temperature. The resulting mixture was warmed up to 50 °C and stirred for 18 hours. The reaction was then cooled to room temperature, quenched with $NaHCO_3$ solution (saturated), extracted with EA (3 times). The extract was washed with brine, dried with sodium sulfate, concentrated *in vacuo* and purified by column chromatography (EA/hexane or MeOH/DCM) to afford the uncyclized product.

General procedure for cyclization: a solution of uncyclized nitro-containing compound (1 equiv.) and palladium on carbon (10 wt.% Pd on carbon, wet, 0.05 equiv.) in solvent mixture of EA and ethanol (1:1, 0.1 M) was stirred at 25 °C under an atmosphere of hydrogen gas for 4 hours. The reaction flask was then purged with argon to replace hydrogen followed by the addition of ammonium formate (1 equiv.). The resulting mixture was warmed up to 40 °C and stirred for 18 hours. The suspension was then filtered through a Celite pad and the filtrate was concentrated *in vacuo* and purified by column chromatography (EA/hexane or MeOH/DCM) to afford the cyclized product.

E. Biochemical and biophysical assays

Thermal shfit Assay:

Florescence thermal shift experiments were performed on a 480 Roche Lightcycler in a 384 well format. The fragments were tested at 2.5 mM with 2.5 % DMSO. The optimal condition was determined to be 0.12 mg/mL GSK3β and 1:400 dilution of Sypro Orange from the original stock. The assay was performed with final volume of 5 µL using a buffer solution containing 50 mM HEPES (pH 7.5) and 150 mM NaCl. Fragments that gave a thermal shift greater 0.5 ^{o}C were considered hits.

Isothermal Titration Calorimetry:

ITC experiments were performed on an ITC_{200} instruments from Microcal Inc. (GE Healthcare) at 25 °C. ITC cell was loaded with GSK3β in concentrations of 50-85 µM with 2-5 % DMSO solution. Ligands were tested at 0.5-2 mM concentrations. Typically, 18 injections of 2.4 µL ligand were performed over a period of 30 min with stirring at 1000 rpm.

Biochemical assay:

The assay kit was acquired from Promega V9103, ADP Glo.

First, 4 µL/well of CABPE, 2 µL of ATP (Promega V9103 component, in AB, 125 mM concentration), and 4 µL of ligand (2.5 mM in AB with 5% DMSO), DMSO (5% in AB), or positive control (GW8510, 20 µM in AB with 5% DMSO) was dispensed into respective wells of a 384-well plate (Corning 3572) to start the reaction. The reaction was

incubated at room temperature for 20 minutes. Second, 10 μL/well of ADP-Glo reagent was added to terminate the reaction. The plate was incubated at room temperature for 40 minutes. Last, 20 μL/well of kinase detection reagent was added. After 30 minutes incubation at room temperature, luminescence was read on an Envision (PerkinElmer) plate reader.

Buffer conditions: AB: 25 mM tris(hydroxymethyl)aminomethane, 10 mM magnesium chloride, pH adjusted to 7.5. CABPE (in AB): 12.5 mM dithiothreitol (Sigma 43816), 0.25 mg/mL bovine serum albumin (Sigma A4503), 0.5 U/mL heparin (Baxter NDC 0641-2440-41), 8 μM GSM (GSK3 substrate peptide, Millipore 12-533), 9 nM GSK3beta (XTAL Biostructures).

NMR experiments:

All spectra were recorded at 298 K on a Bruker Avance 600 MHz NMR spectrometer equipped with z-axis gradients. The data were collected with a sweep width of 12019 Hz and 8192 complex points. For each sample 1D 1H, STD,[90] and WaterLOGSY[91] spectra were collected with water suppression using excitation sculpting.[92] The 1D ^{1}H spectrum was acquired with 128 scans and a relaxation delay of 1.5s. The STD experiment was acquired with a 3s saturation period (50ms Gaussian shaped pulse), a recycle delay of 0.5s and 256 scans each for the on-resonance (0.8ppm) and off-resonance (-25ppm). The WaterLOGSY experiment was acquired with 512 scans, a mixing time of 2.3s, and a recycle delay of 1.3s. The relaxation-edited experiment was acquired with 256 scans, a recycle delay of 2s and a 300ms CPMG spin-lock period. All spectra were processed

using nmrPipe[93] and prior to Fourier transformation the data were multiplied by and shifted sine-bell weighting function and an exponential function with a line broadening of 0.5Hz.

References

(1) Schreiber, S. L. *Nature* **2009**, *457*, 153.

(2) Schreiber, S. L. *Nat. Chem. Biol.* **2005**, *1*, 64.

(3) Schreiber, S. L. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 6699.

(4) Stockwell, B. R. *Nature* **2004**, *432*, 846.

(5) Broach, J. R.; Thorner, J. *Nature (London)* **1996**, *384*, 14.

(6) Diller, D. J. *Curr. Opin. Drug Discovery Dev.* **2008**, *11*, 346.

(7) Hertzberg, R. P.; Pope, A. J. *Curr. Opin. Chem. Biol.* **2000**, *4*, 445.

(8) Hill, D. C. *Curr. Opin. Drug Discovery Dev.* **1998**, *1*, 92.

(9) Inglese, J.; Johnson, R. L.; Simeonov, A.; Xia, M.; Zheng, W.; Austin, C. P.; Auld, D. S. *Nat. Chem. Biol.* **2007**, *3*, 466.

(10) Macarron, R.; Banks, M. N.; Bojanic, D.; Burns, D. J.; Cirovic, D. A.; Garyantes, T.; Green, D. V. S.; Hertzberg, R. P.; Janzen, W. P.; Paslay, J. W.; Schopfer, U.; Sittampalam, G. S. *Nat. Rev. Drug Discovery Dev.* **2011**, *10*, 188.

(11) Posner, B. A. *Curr. Opin. Drug Discovery Dev.* **2005**, *8*, 487.

(12) Clemons, P. A.; Wilson, J. A.; Dancik, V.; Muller, S.; Carrinski, H. A.; Wagner, B. K.; Koehler, A. N.; Schreiber, S. L. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 6817.

(13) Clemons, P. A.; Bodycombe, N. E.; Carrinski, H. A.; Wilson, J. A.; Shamji, A. F.; Wagner, B. K.; Koehler, A. N.; Schreiber, S. L. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 18787.

(14) Bohacek, R. S.; McMartin, C.; Guida, W. C. *Med. Res. Rev.* **1996**, *16*, 3.

(15) Payne, D. J.; Gwynn, M. N.; Holmes, D. J.; Pompliano, D. L. *Nat. Rev. Drug Discov.* **2007**, *6*, 29.

(16) Feher, M.; Schmidt, J. M. *J. Chem. Inf. Comput. Sci.* **2002**, *43*, 218.

(17) Congreve, M.; Chessari, G.; Tisi, D.; Woodhead, A. J. *J. Med. Chem.* **2008**, *51*, 3661.

(18) Fattori, D.; Squarcia, A.; Bartoli, S. *Drugs R D* **2008**, *9*, 217.

(19) Erlanson, D. A.; McDowell, R. S.; O'Brien, T. *J. Med. Chem.* **2004**, *47*, 3463.

(20) Erlanson, D. A.; Wells, J. A.; Braisted, A. C. *Annu. Rev. Biophys. Biomol. Struct.* **2004**, *33*, 199.

(21) Bembenek, S. D.; Tounge, B. A.; Reynolds, C. H. *Drug Discov. Today* **2009**, *14*, 278.

(22) Murray, C. W.; Rees, D. C. *Nat. Chem.* **2009**, *1*, 187.

(23) van Montfort, R. L.; Collins, I. *Curr. Top. Med. Chem.* **2009**, *9*, 1676.

(24) Chessari, G.; Woodhead, A. J. *Drug Discov. Today* **2009**, *14*, 668.

(25) Fink, T.; Bruggesser, H.; Reymond, J. L. *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 1504.

(26) Fink, T.; Reymond, J. L. *J. Chem. Inf. Model.* **2007**, *47*, 342.

(27) Ciulli, A.; Abell, C. *Curr. Opin. Biotechnol.* **2007**, *18*, 489.

(28) Hung, A. W.; Silvestre, H. L.; Wen, S.; Ciulli, A.; Blundell, T. L.; Abell, C. *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 8452.

(29) Barker, J. J.; Barker, O.; Courtney, S. M.; Gardiner, M.; Hesterkamp, T.; Ichihara, O.; Mather, O.; Montalbetti, C. A.; Muller, A.; Varasi, M.; Whittaker, M.; Yarnold, C. J. *ChemMedChem* **2010**, *5*, 1697.

(30) Borsi, V.; Calderone, V.; Fragai, M.; Luchinat, C.; Sarti, N. *J. Med. Chem.* **2010**, *53*, 4285.

(31) Edink, E.; Rucktooa, P.; Retra, K.; Akdemir, A.; Nahar, T.; Zuiderveld, O.; van Elk, R.; Janssen, E.; van Nierop, P.; van Muijlwijk-Koezen, J.; Smit, A. B.; Sixma, T. K.; Leurs, R.; de Esch, I. J. *J. Am. Chem. Soc.* **2011**, *133*, 5363.

(32) Howard, N.; Abell, C.; Blakemore, W.; Chessari, G.; Congreve, M.; Howard, S.; Jhoti, H.; Murray, C. W.; Seavers, L. C.; van Montfort, R. L. *J. Med. Chem.* **2006**, *49*, 1346.

(33) Nazare, M.; Matter, H.; Will, D. W.; Wagner, M.; Urmann, M.; Czech, J.; Schreuder, H.; Bauer, A.; Ritter, K.; Wehner, V. *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 905.

(34) Rohrig, C. H.; Loch, C.; Guan, J. Y.; Siegal, G.; Overhand, M. *ChemMedChem* **2007**, *2*, 1054.

(35) Sledz, P.; Silvestre, H. L.; Hung, A. W.; Ciulli, A.; Blundell, T. L.; Abell, C. *J. Am. Chem. Soc.* **2010**, *132*, 4544.

(36) Blundell, T. L.; Jhoti, H.; Abell, C. *Nat. Rev. Drug Discov.* **2002**, *1*, 45.

(37) Drinkwater, N.; Vu, H.; Lovell, K. M.; Criscione, K. R.; Collins, B. M.; Prisinzano, T. E.; Poulsen, S. A.; McLeish, M. J.; Grunewald, G. L.; Martin, J. L. *Biochem. J.* **2010**, *431*, 51.

(38) Hennig, M.; Ruf, A.; Huber, W. *Top. Curr. Chem.* **2012**, *317*, 115.

(39) Verlinde, C. L.; Fan, E.; Shibata, S.; Zhang, Z.; Sun, Z.; Deng, W.; Ross, J.; Kim, J.; Xiao, L.; Arakaki, T. L.; Bosch, J.; Caruthers, J. M.; Larson, E. T.; Letrong, I.; Napuli, A.; Kelly, A.; Mueller, N.; Zucker, F.; Van Voorhis, W. C.; Buckner, F. S.; Merritt, E. A.; Hol, W. G. *Curr. Top. Med. Chem.* **2009**, *9*, 1678.

(40) Wang, Y. S.; Strickland, C.; Voigt, J. H.; Kennedy, M. E.; Beyer, B. M.; Senior, M. M.; Smith, E. M.; Nechuta, T. L.; Madison, V. S.; Czarniecki, M.; McKittrick, B. A.; Stamford, A. W.; Parker, E. M.; Hunter, J. C.; Greenlee, W. J.; Wyss, D. F. *J. Med. Chem.* **2010**, *53*, 942.

(41) Wyss, D. F.; Wang, Y. S.; Eaton, H. L.; Strickland, C.; Voigt, J. H.; Zhu, Z.; Stamford, A. W. *Top. Curr. Chem.* **2012**, *317*, 83.

(42) Gill, A.; Cleasby, A.; Jhoti, H. *Chembiochem* **2005**, *6*, 506.

(43) Hartshorn, M. J.; Murray, C. W.; Cleasby, A.; Frederickson, M.; Tickle, I. J.; Jhoti, H. *J. Med. Chem.* **2005**, *48*, 403.

(44) Jhoti, H.; Cleasby, A.; Verdonk, M.; Williams, G. *Curr. Opin. Chem. Biol.* **2007**, *11*, 485.

(45) Wyatt, P. G.; Woodhead, A. J.; Berdini, V.; Boulstridge, J. A.; Carr, M. G.; Cross, D. M.; Davis, D. J.; Devine, L. A.; Early, T. R.; Feltell, R. E.; Lewis, E. J.; McMenamin, R. L.; Navarro, E. F.; O'Brien, M. A.; O'Reilly, M.; Reule, M.; Saxty, G.; Seavers, L. C.; Smith, D. M.; Squires, M. S.; Trewartha, G.; Walker, M. T.; Woolford, A. J. *J. Med. Chem.* **2008**, *51*, 4986.

(46) Hajduk, P. J.; Galloway, W. R.; Spring, D. R. *Nature* **2011**, *470*, 42.

(47) Hajduk, P. J.; Greer, J. *Nat. Rev. Drug. Discov.* **2007**, *6*, 211.

(48) Coyne, A. G.; Scott, D. E.; Abell, C. *Curr. Opin. Chem. Biol.* **2010**, *14*, 299.

(49) Lovering, F.; Bikker, J.; Humblet, C. *J. Med. Chem.* **2009**, *52*, 6752.

(50) Ritchie, T. J.; Macdonald, S. J. *Drug Discov. Today* **2009**, *14*, 1011.

(51) Ritchie, T. J.; Macdonald, S. J.; Young, R. J.; Pickett, S. D. *Drug Discov. Today* **2011**, *16*, 164.

(52) May, P. C.; Dean, R. A.; Lowe, S. L.; Martenyi, F.; Sheehan, S. M.; Boggs, L. N.; Monk, S. A.; Mathes, B. M.; Mergott, D. J.; Watson, B. M.; Stout, S. L.; Timm, D. E.;

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(53) Kumagai, N.; Muncipinto, G.; Schreiber, S. L. *Angew. Chem. Int. Ed.* **2006**, *45*, 3635.

(54) Spiegel, D. A.; Schroeder, F. C.; Duvall, J. R.; Schreiber, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 14766.

(55) Nielsen, T. E.; Schreiber, S. L. *Angew. Chem. Int. Ed.***2008**, *47*, 48.

(56) Luo, T. P.; Schreiber, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 5667.

(57) Uchida, T.; Rodriquez, M.; Schreiber, S. L. *Org. Lett.* **2009**, *11*, 1559.

(58) Dandapani, S.; Marcaurelle, L. A. *Curr. Opin. Chem. Biol.* **2010**, *14*, 362.

(59) Marcaurelle, L. A.; Comer, E.; Dandapani, S.; Duvall, J. R.; Gerard, B.; Kesavan, S.; Lee, M. D. t.; Liu, H.; Lowe, J. T.; Marie, J. C.; Mulrooney, C. A.; Pandya, B. A.; Rowley, A.; Ryba, T. D.; Suh, B. C.; Wei, J.; Young, D. W.; Akella, L. B.; Ross, N. T.; Zhang, Y. L.; Fass, D. M.; Reis, S. A.; Zhao, W. N.; Haggarty, S. J.; Palmer, M.; Foley, M. A. *J. Am. Chem. Soc.* **2010**, *132*, 16962.

(60) Muncipinto, G.; Kaya, T.; Wilson, J. A.; Kumagai, N.; Clemons, P. A.; Schreiber, S. L. *Org. Lett.* **2010**, *12*, 5230.

(61) Pizzirani, D.; Kaya, T.; Clemons, P. A.; Schreiber, S. L. *Org. Lett.* **2010**, *12*, 2822.

(62) Akella, L. B.; Marcaurelle, L. A. *ACS Comb. Sci.* **2011**, *13*, 357.

(63) Chou, D. H. C.; Duvall, J. R.; Gerard, B.; Liu, H. B.; Pandya, B. A.; Suh, B. C.; Forbeck, E. M.; Faloon, P.; Wagner, B. K.; Marcaurelle, L. A. *ACS Med. Chem. Lett.* **2011**, *2*, 698.

(64) Dandapani, S.; Lowe, J. T.; Comer, E.; Marcaurelle, L. A. *J. Org. Chem.* **2011**, *76*, 8042.

(65) Gerard, B.; Duvall, J. R.; Lowe, J. T.; Murillo, T.; Wei, J.; Akella, L. B.; Marcaurelle, L. A. *ACS Comb. Sci.* **2011**, *13*, 365.

(66) Kramer, C.; Gedeck, P. *J. Chem. Inf. Model* **2011**, *51*, 2139.

(67) Pandya, B. A.; Dandapani, S.; Duvall, J. R.; Rowley, A.; Mulrooney, C. A.; Ryba, T.; Dombrowski, M.; Harton, M.; Young, D. W.; Marcaurelle, L. A. *Tetrahedron* **2011**, *67*, 6131.

(68) Samarakoon, T. B.; Loh, J. K.; Rolfe, A.; Le, L. S.; Yoon, S. Y.; Lushington, G. H.; Hanson, P. R. *Org. Lett.* **2011**, *13*, 5148.

(69) Fitzgerald, M. E.; Mulrooney, C. A.; Duvall, J. R.; Wei, J.; Suh, B. C.; Akella, L. B.; Vrcic, A.; Marcaurelle, L. A. *ACS Comb. Sci.* **2012**.

(70) Harris, P. W. R.; Brimble, M. A.; Gluckman, P. D. *Org. Lett.* **2003**, *5*, 1847.

(71) Seebach, D.; Boes, M.; Naef, R.; Schweizer, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 5390.

(72) Wang, H.; Germanas, J. P. *Synlett* **1999**, 33.

(73) Huang, P. Q. *Synlett* **2006**, 1133.

(74) Harris, P. W. R.; Brimble, M. A. *Org. Biomol. Chem.* **2006**, *4*, 2696.

(75) Hoffmann, T.; Lanig, H.; Waibel, R.; Gmeiner, P. *Angew. Chem. Int. Ed.***2001**, *40*, 3361.

(76) Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414.

(77) McNaughton, B. R.; Bucholtz, K. M.; Camaano-Moure, A.; Miller, B. L. *Org. Lett.* **2005**, *7*, 733.

(78) Martin, R.; Cuenca, A.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 5521.

(79) Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.* **1989**, *30*, 6051.

(80) Paone, D. V.; Shaw, A. W.; Nguyen, D. N.; Burgey, C. S.; Deng, J. Z.; Kane, S. A.; Koblan, K. S.; Salvatore, C. A.; Mosser, S. D.; Johnston, V. K.; Wong, B. K.; Miller-Stein, C. M.; Hershey, J. C.; Graham, S. L.; Vacca, J. P.; Williams, T. M. *J. Med. Chem.* **2007**, *50*, 5564.

(81) Mao, Y.; Ge, X.; Frank, C. L.; Madison, J. M.; Koehler, A. N.; Doud, M. K.; Tassa, C.; Berry, E. M.; Soda, T.; Singh, K. K.; Biechele, T.; Petryshen, T. L.; Moon, R. T.; Haggarty, S. J.; Tsai, L. H. *Cell* **2009**, *136*, 1017.

(82) Feng, Y.; Lee, N.; Fearon, E. R. *Cancer Res.* **2003**, *63*, 8726.

(83) Lo, M. C.; Aulabaugh, A.; Jin, G.; Cowling, R.; Bard, J.; Malamas, M.; Ellestad, G. *Anal. Biochem.* **2004**, *332*, 153.

(84) Ojo, K. K.; Gillespie, J. R.; Riechers, A. J.; Napuli, A. J.; Verlinde, C. L. M. J.; Buckner, F. S.; Gelb, M. H.; Domostoj, M. M.; Wells, S. J.; Scheer, A.; Wells, T. N. C.; Van Voorhis, W. C. *Antimicrob. Agents Chemother.* **2008**, *52*, 3710.

(85) Tanimori, S.; Kashiwagi, H.; Nishimura, T.; Kirihata, M. *Adv. Synth. Catal.* **2010**, *352*, 2531.

(86) Gould, A. E.; Adams, R.; Adhikari, S.; Aertgeerts, K.; Afroze, R.; Blackburn, C.; Calderwood, E. F.; Chau, R.; Chouitar, J.; Duffey, M. O.; England, D. B.; Farrer, C.; Forsyth, N.; Garcia, K.; Gaulin, J.; Greenspan, P. D.; Guo, R.; Harrison, S. J.; Huang, S.-C.; Iartchouk, N.; Janowick, D.; Kim, M.-S.; Kulkarni, B.; Langston, S. P.; Liu, J. X.; Ma, L.-T.; Menon, S.; Mizutani, H.; Paske, E.; Renou, C. C.; Rezaei, M.; Rowland, R. S.; Sintchak, M. D.; Smith, M. D.; Stroud, S. G.; Tregay, M.; Tian, Y.; Veiby, O. P.; Vos, T. J.; Vyskocil, S.; Williams, J.; Xu, T.; Yang, J. J.; Yano, J.; Zeng, H.; Zhang, D. M.; Zhang, Q.; Galvin, K. M. *J. Med. Chem.* **2011**, *54*, 1836.

(87) Ramnauth, J.; Surman, M. D.; Sampson, P. B.; Forrest, B.; Wilson, J.; Freeman, E.; Manning, D. D.; Martin, F.; Toro, A.; Domagala, M.; Awrey, D. E.; Bardouniotis, E.; Kaplan, N.; Berman, J.; Pauls, H. W. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 5359.

(88) Sampson, P. B.; Picard, C.; Handerson, S.; McGrath, T. E.; Domagala, M.; Leeson, A.; Romanov, V.; Awrey, D. E.; Thambipillai, D.; Bardouniotis, E.; Kaplan, N.; Berman, J. M.; Pauls, H. W. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 5355.

(89) Chen, J. J.; Qian, W.; Biswas, K.; Viswanadhan, V. N.; Askew, B. C.; Hitchcock, S.; Hungate, R. W.; Arik, L.; Johnson, E. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4477.

(90) Mayer, M.; Meyer, B. *Angew. Chem. Int. Ed.***1999**, *38*, 1784.

(91) Dalvit, C.; Fogliatto, G.; Stewart, A.; Veronesi, M.; Stockman, B. *J. Biomol. NMR* **2001**, *21*, 349.

(92) Hwang, T. L.; Shaka, A. J. *J. Magn. Reson. Ser. A* **1995**, *112*, 275.

(93) Delaglio, F.; Grzesiek, S.; Vuister, G. W.; Zhu, G.; Pfeifer, J.; Bax, A. *J. Biomol. NMR* **1995**, *6*, 277.

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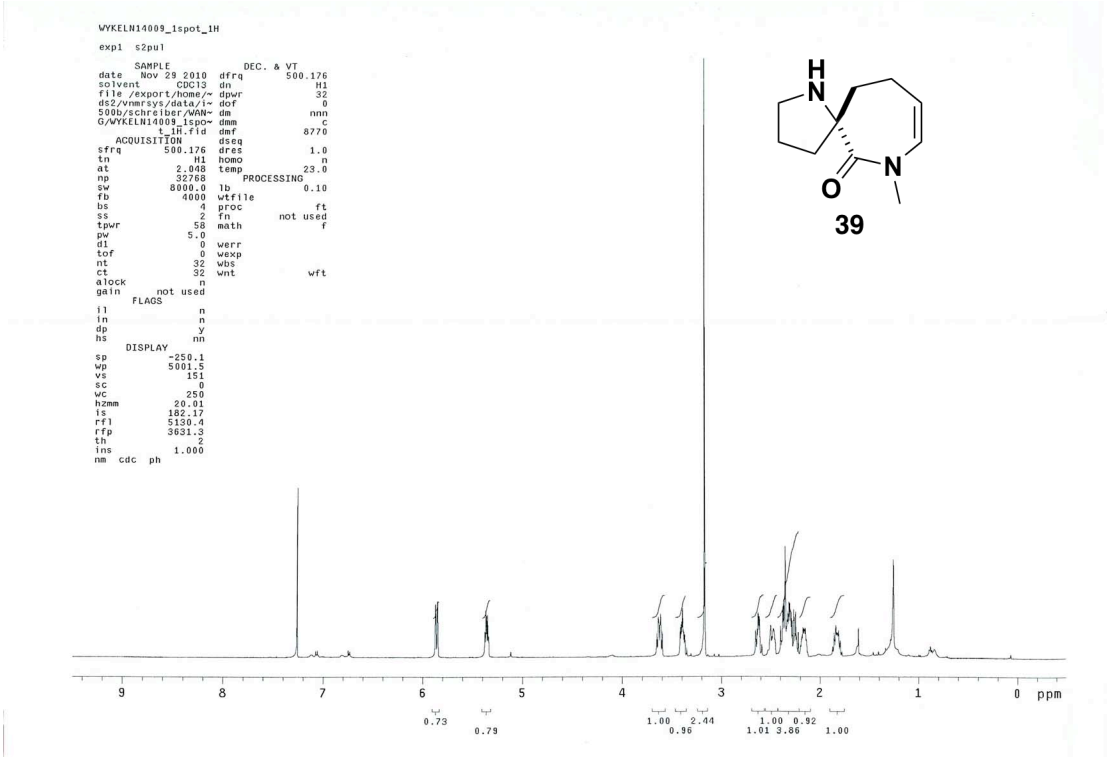

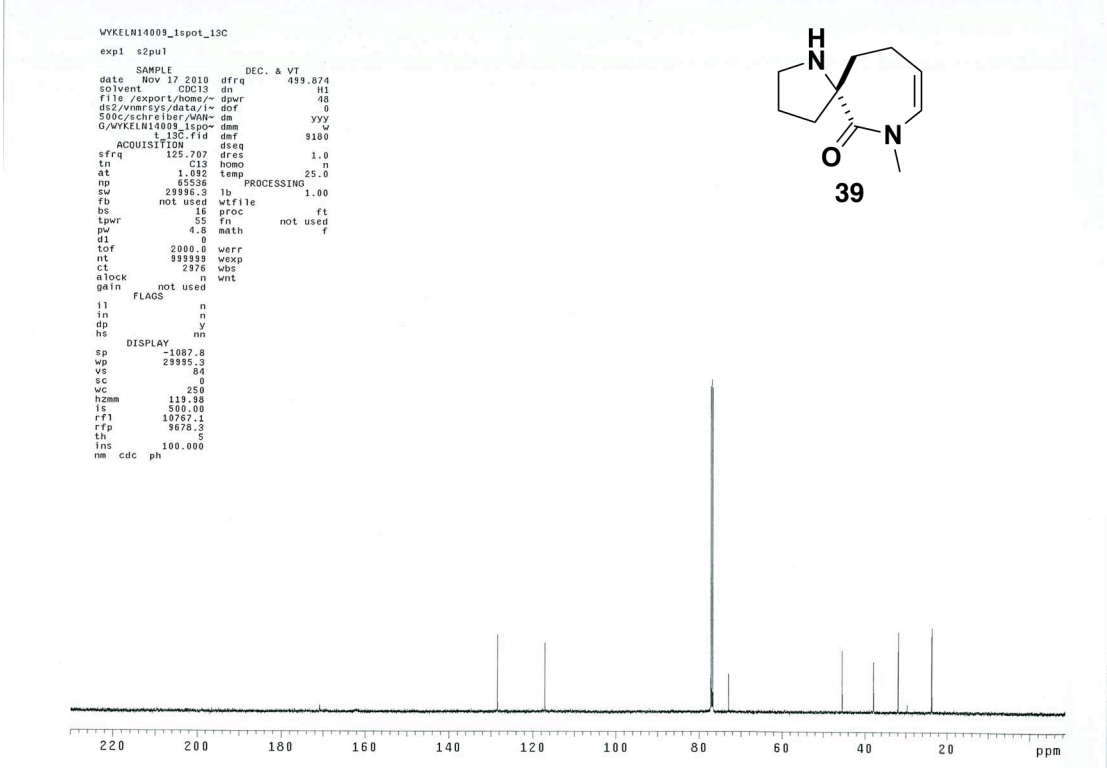

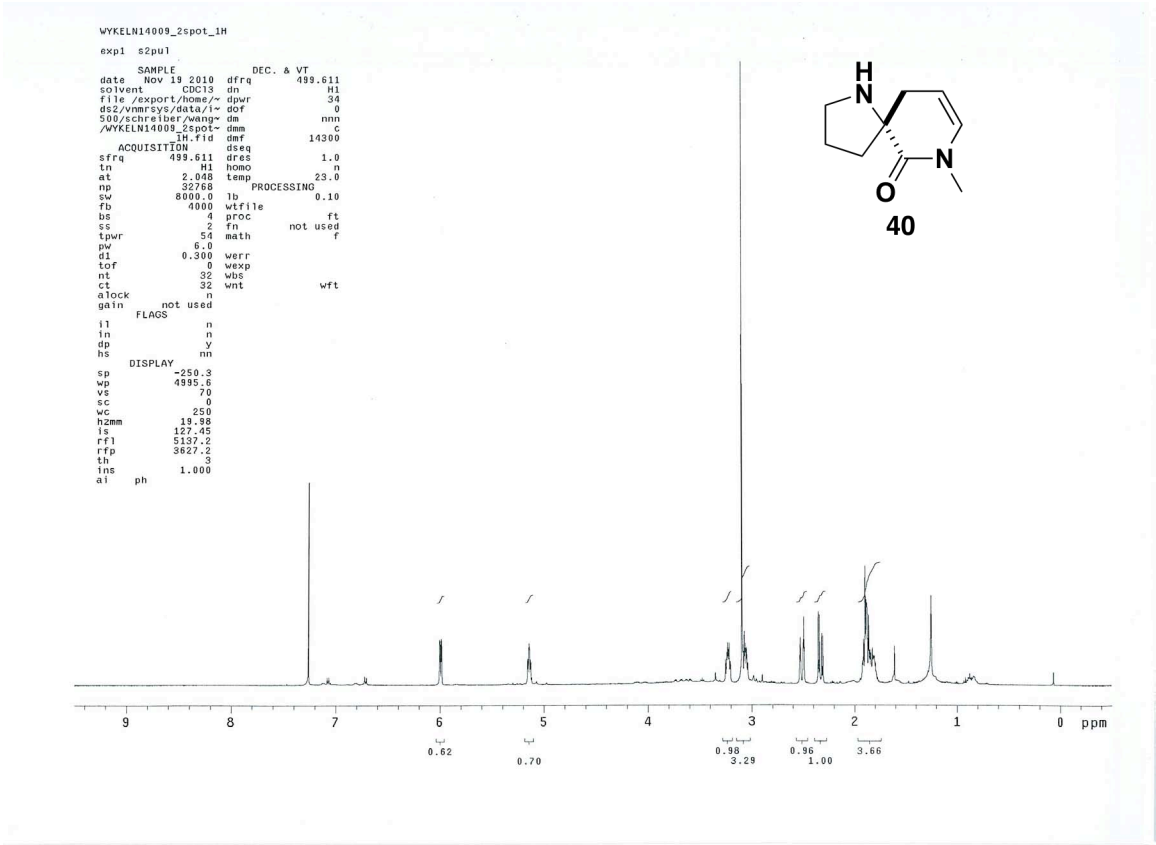
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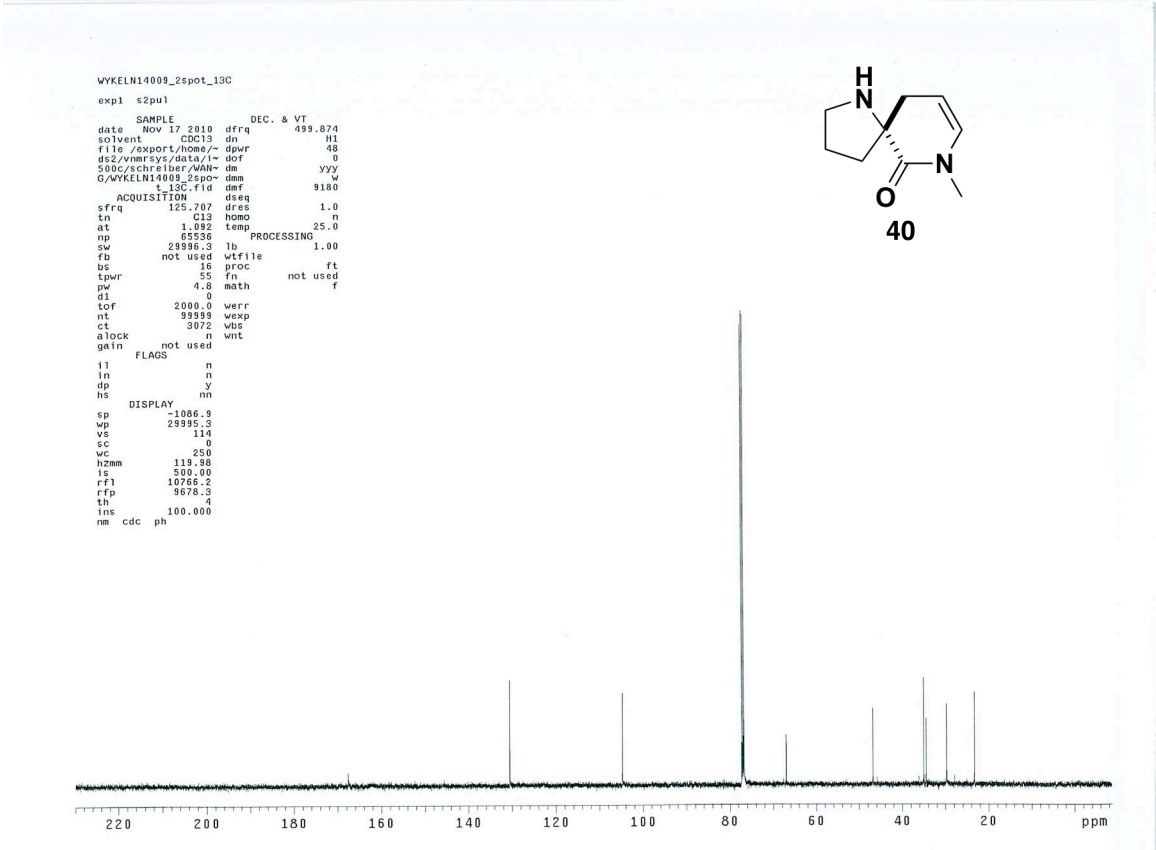
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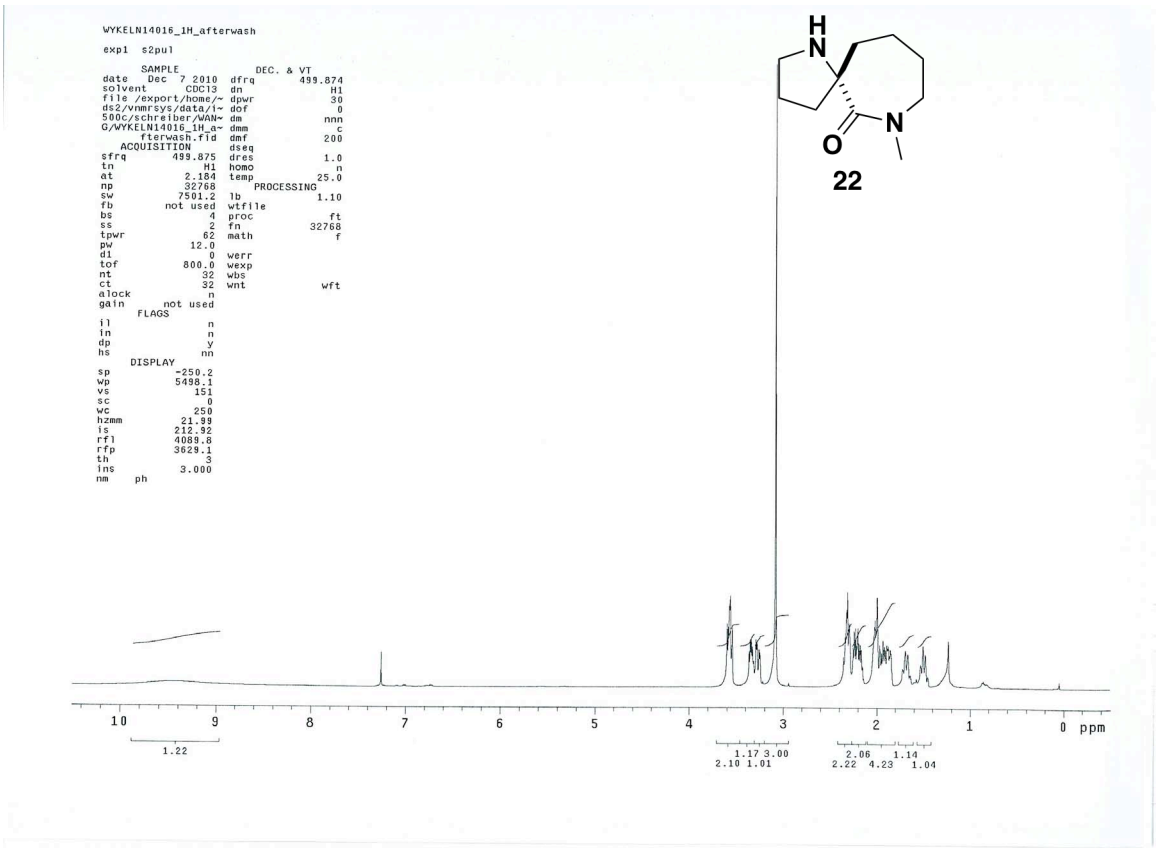
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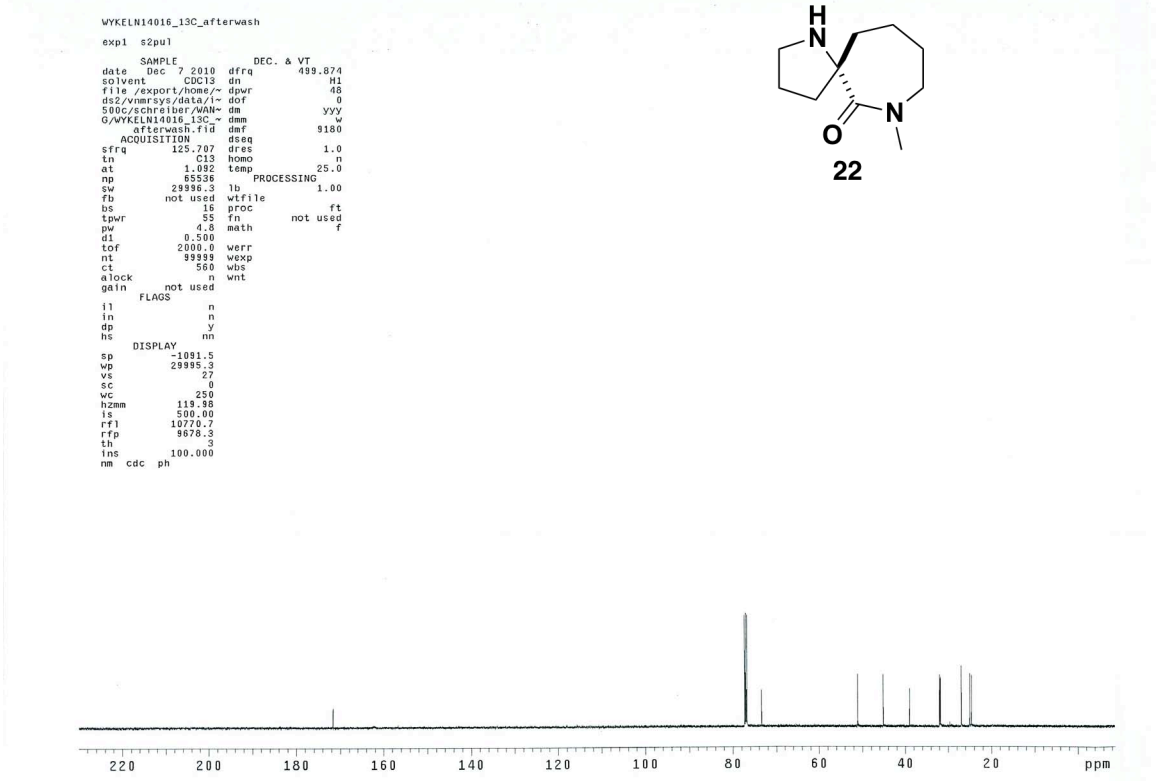
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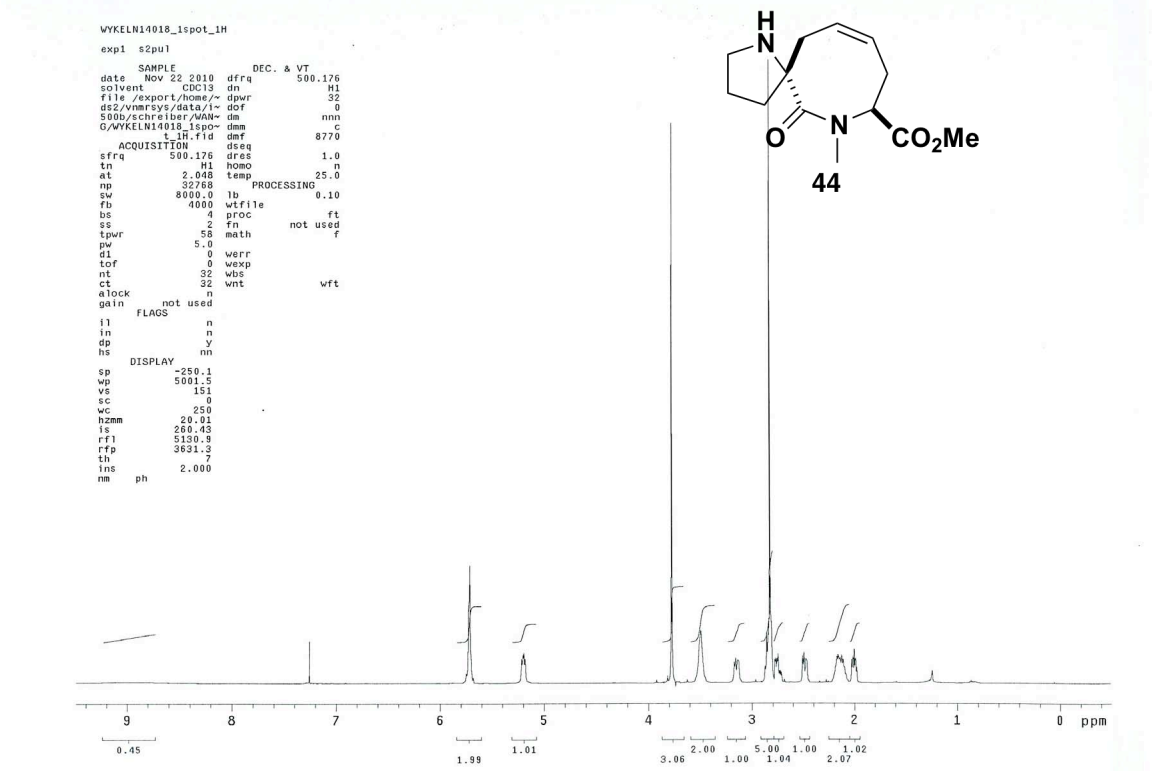
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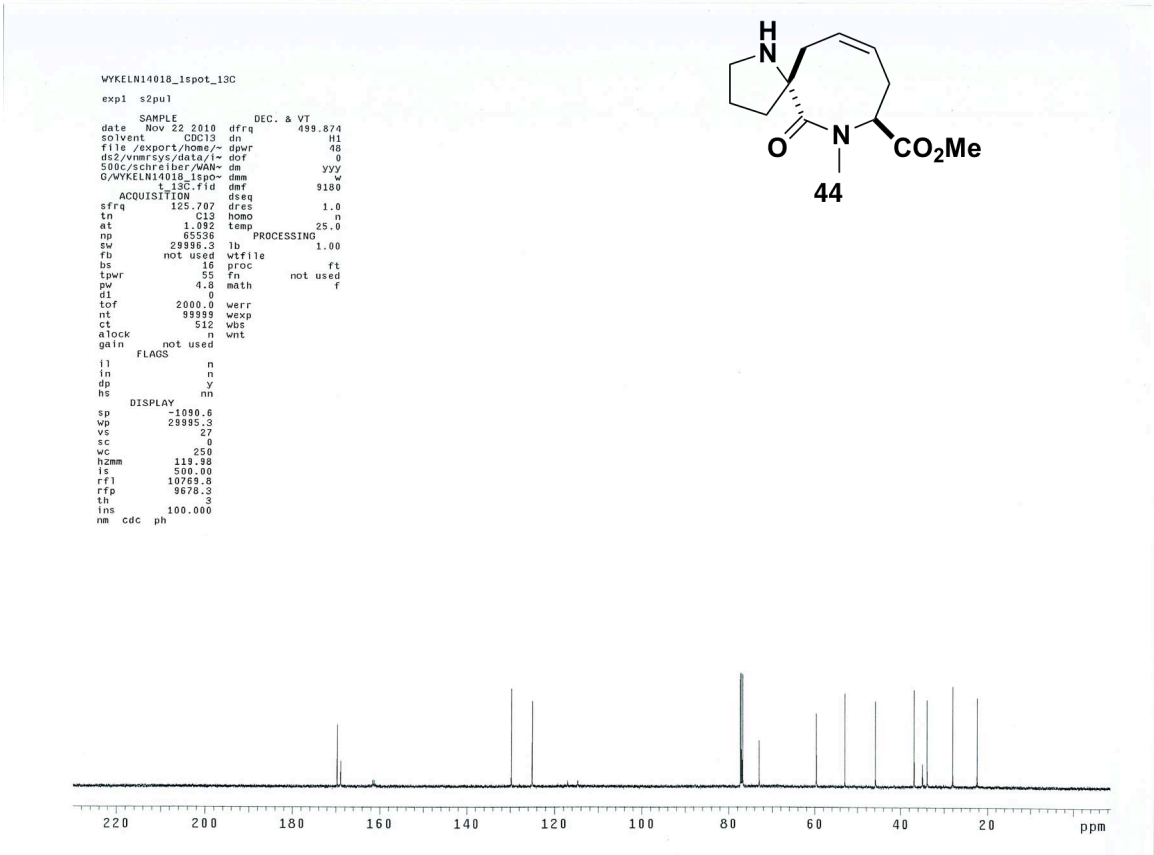
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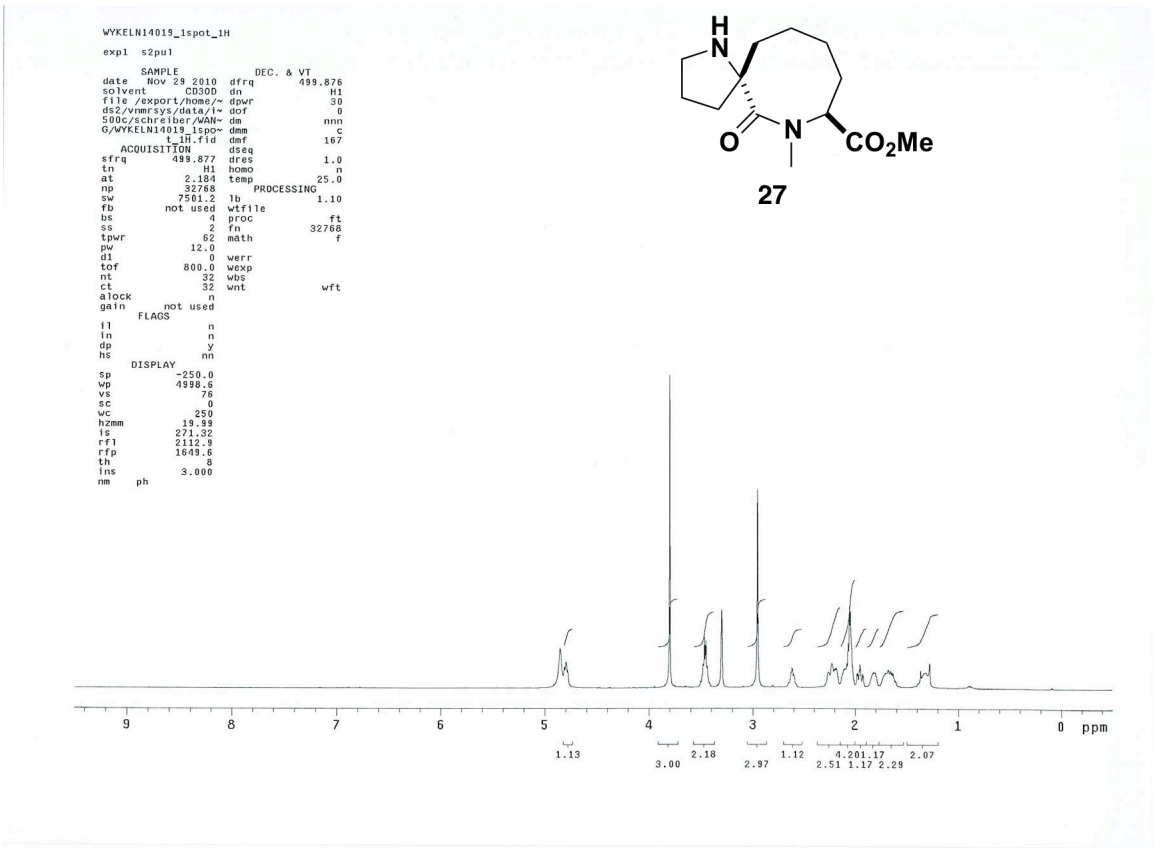
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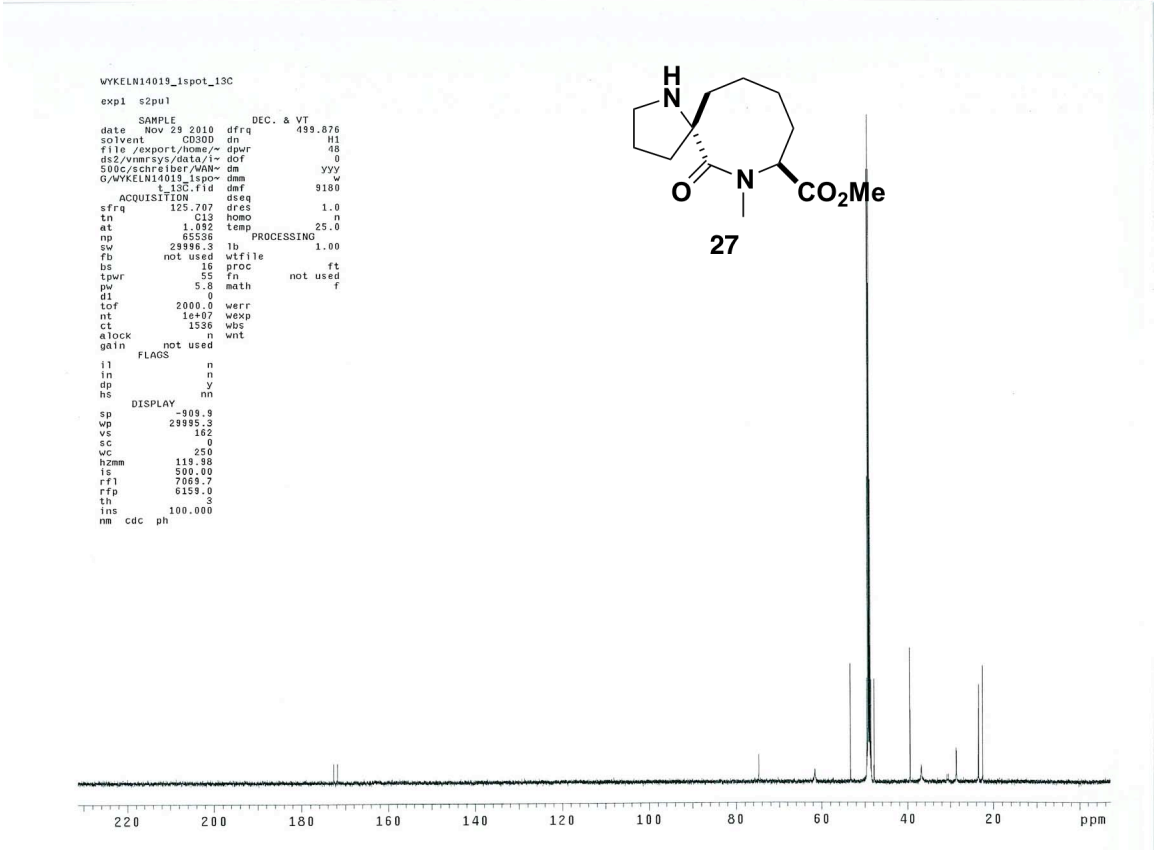
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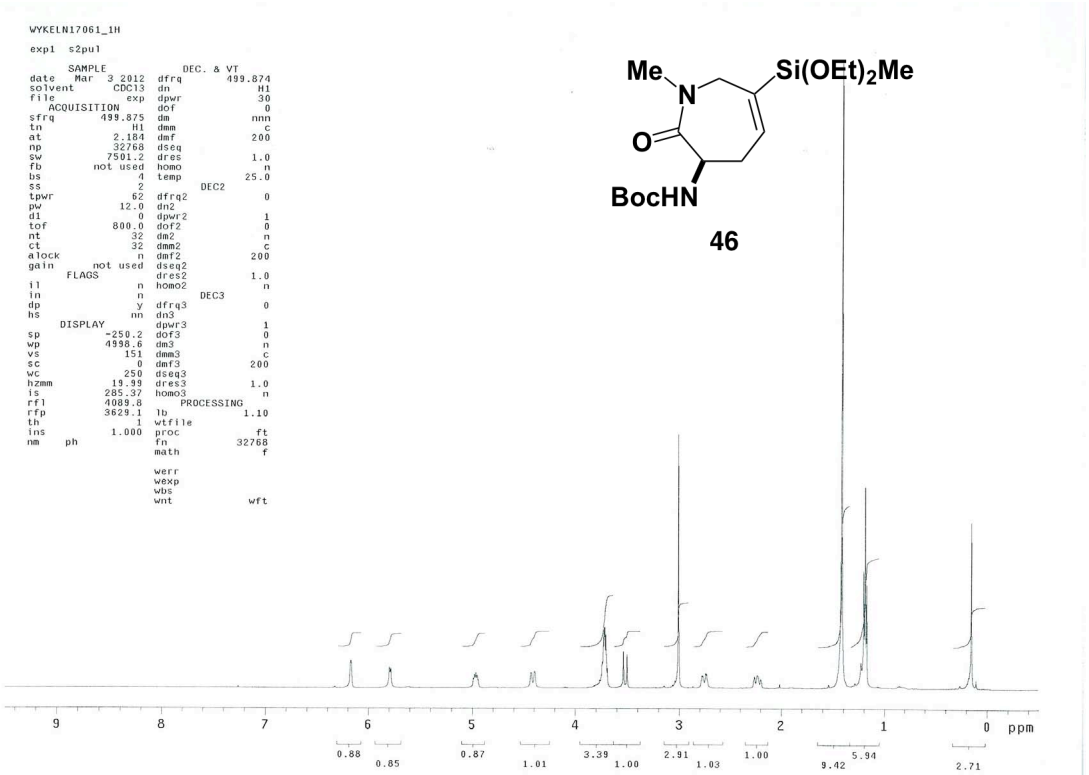
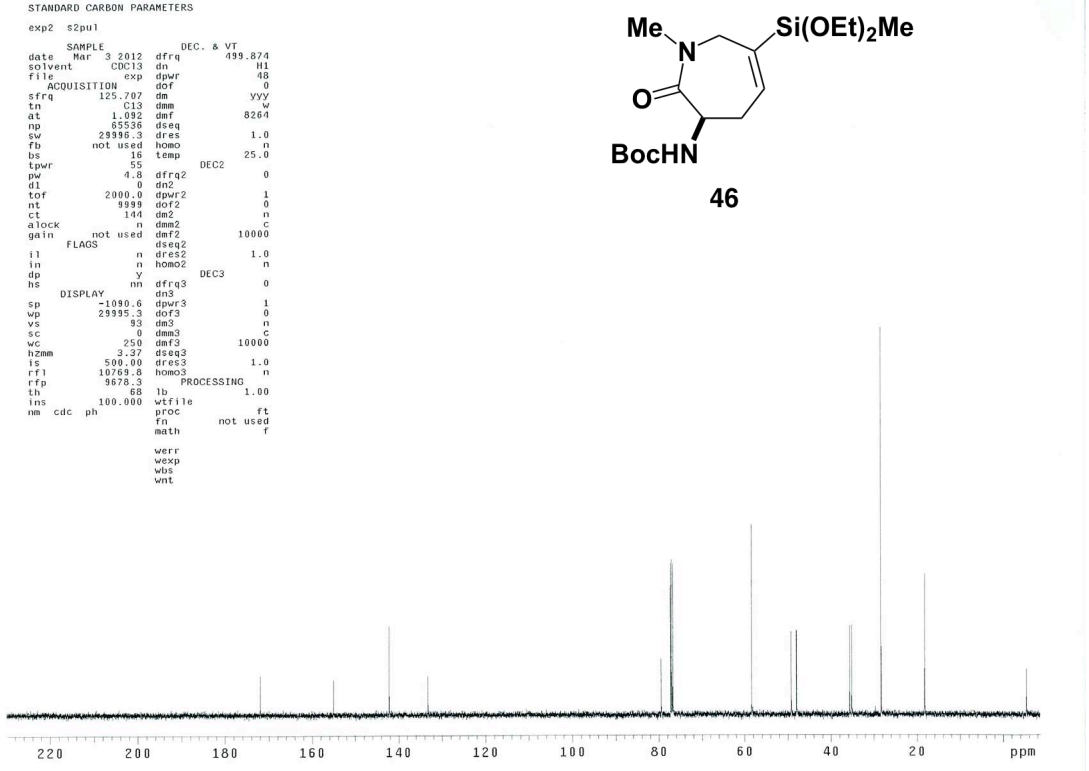
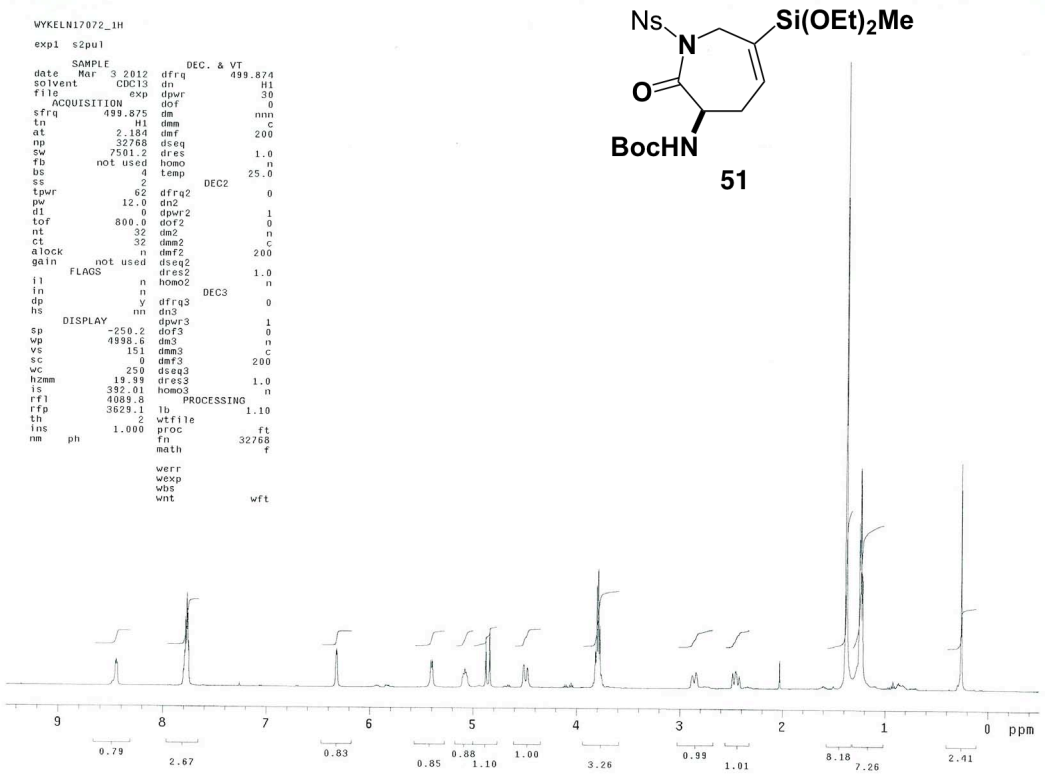
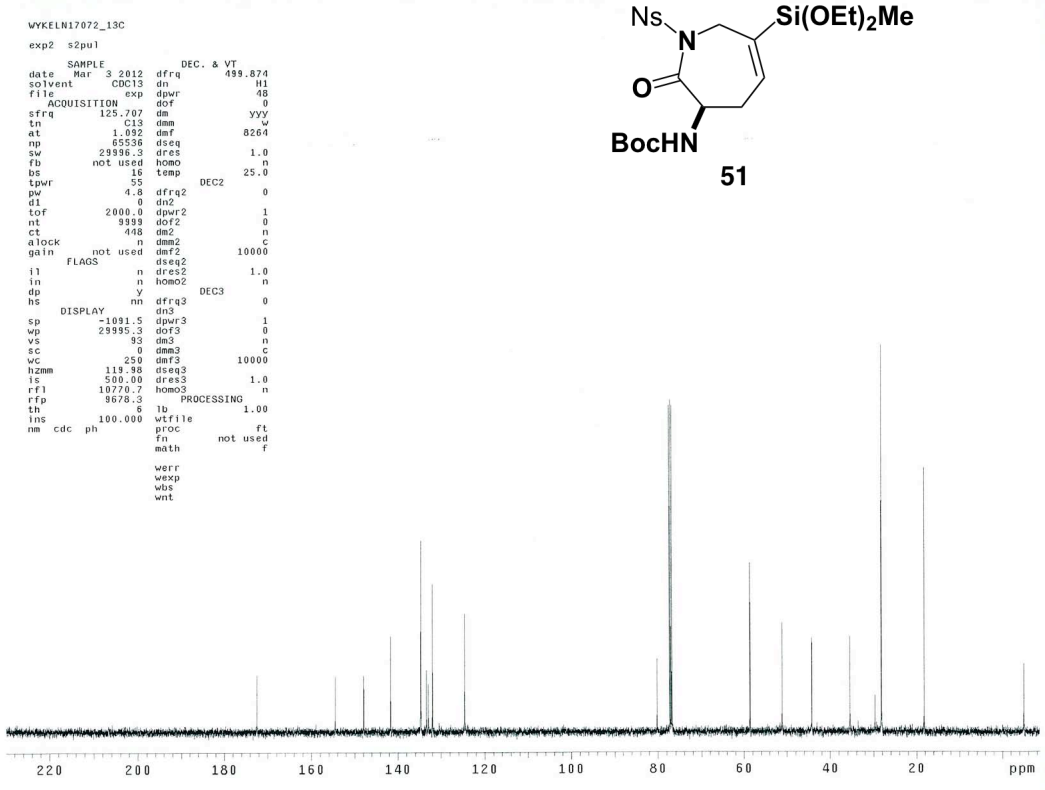
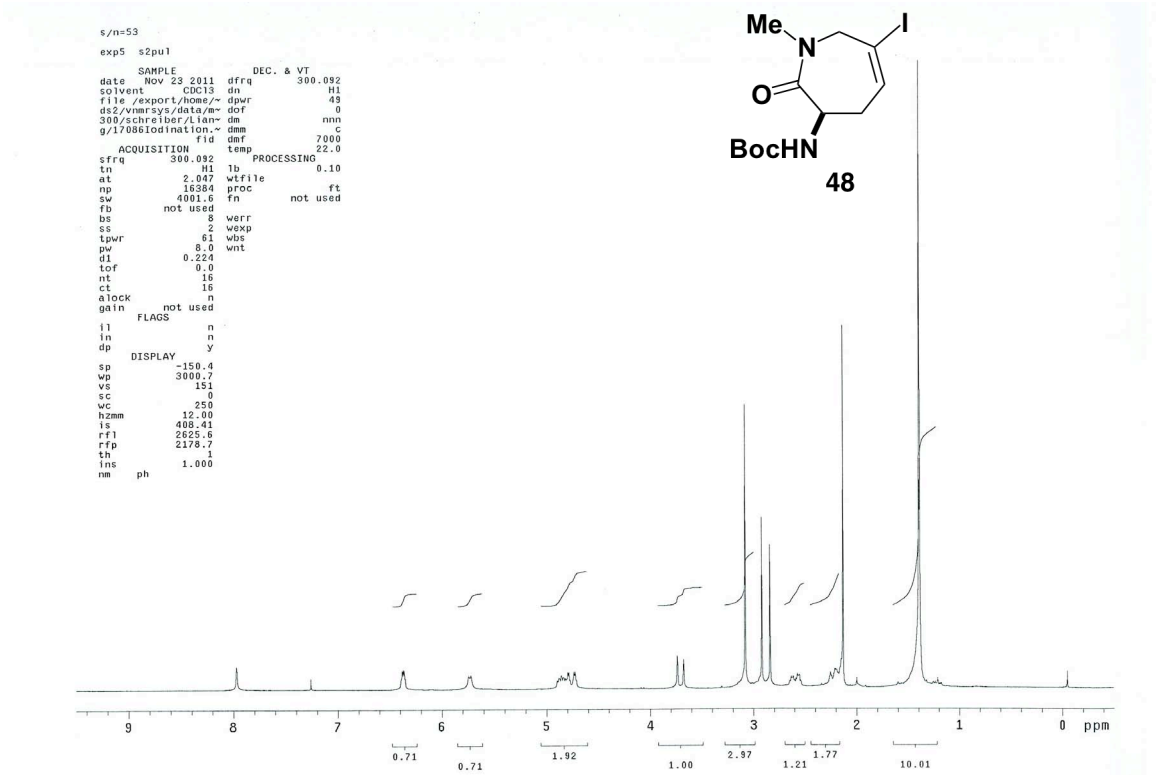
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
H
N
O
N
CO2Me
27
220
200
180
160
140
120
100
80
60
40
20
ppm

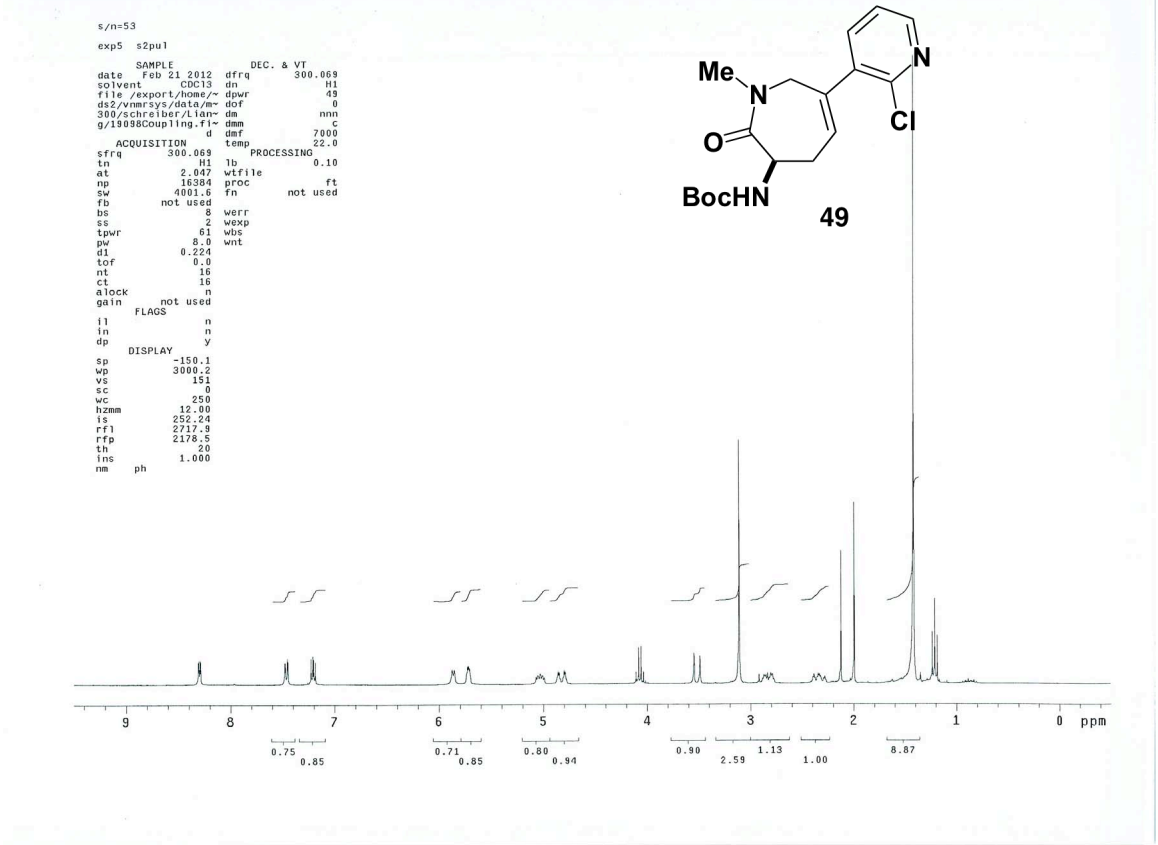

WYKELN17061_1H
exp1 s2pul
SAMPLE
date Mar 3 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 285.37
rfl 4089.8
rfp 3629.1
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
Me
N
Si(OEt)2Me
O
BocHN
46
9
8
7
6
5
4
3
2
1
0
ppm
0.88
0.85
0.87
1.01
3.39
1.00
2.91
1.03
1.00
9.42
5.94
2.71


STANDARD CARBON PARAMETERS
exp2 s2pul
SAMPLE
date Mar 3 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 144
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1090.6
wp 29995.3
vs 93
sc 0
wc 250
hzmm 3.37
is 500.00
rfl 10769.8
rfp 9678.3
th 68
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8264
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Me
N
Si(OEt)2Me
O
BocHN
46
220
200
180
160
140
120
100
80
60
40
20
ppm


WYKELN17072_1H
exp1 s2pul
SAMPLE
date Mar 3 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 4
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 151
sc 0
wc 250
hzmm 19.99
is 382.01
rfl 4089.8
rfp 3629.1
th 2
ins 1.000
nm ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
Ns
N
O
BocHN
Si(OEt)2Me
51
9
8
7
6
5
4
3
2
1
0
ppm
0.79
2.67
0.83
0.85
0.88
1.10
1.00
3.26
0.99
1.01
8.18
7.26
2.41


WYKELN17072_13C
exp2 s2pul
SAMPLE
date Mar 3 2012
solvent CDCl3
file exp
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 16
tpwr 55
pw 4.8
d1 0
tof 2000.0
nt 9999
ct 448
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1091.5
wp 29995.3
vs 93
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 10770.7
rfp 9678.3
th 6
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8264
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Ns
N
O
BocHN
Si(OEt)2Me
51
220
200
180
160
140
120
100
80
60
40
20
ppm

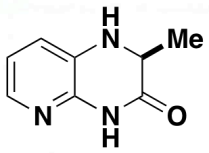

s/n=53
exp5 s2pul
SAMPLE
date Nov 23 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/m~
300/schreiber/Lian~
g/17086Iodination.~
fid
ACQUISITION
sfrq 300.092
tn H1
at 2.047
np 16384
sw 4001.6
fb not used
bs 8
ss 2
tpwr 61
pw 8.0
d1 0.224
tof 0.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -150.4
wp 3000.7
vs 151
sc 0
wc 250
hzmm 12.00
is 408.41
rfl 2625.6
rfp 2178.7
th 1
ins 1.000
nm ph
DEC. & VT
dfrq 300.092
dn H1
dpwr 48
dof 0
dm nnn
dmm c
dmf 7000
temp 22.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
N
I
O
BocHN
48
9
8
7
6
5
4
3
2
1
0 ppm
0.71
0.71
1.92
1.00
2.97
1.21
1.77
10.01


s/n=53
exp5 s2pul
SAMPLE
date Feb 21 2012
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/m~
300/schreiber/Lian~
g/19098Coupling.fi~
d
ACQUISITION
sfrq 300.069
tn H1
at 2.047
np 16384
sw 4001.6
fb not used
bs 8
ss 2
tpwr 61
pw 8.0
d1 0.224
tof 0.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -150.1
wp 3000.2
vs 151
sc 0
wc 250
hzmm 12.00
is 252.24
rfl 2717.9
rfp 2178.5
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 300.069
dn H1
dpwr 49
dof 0
dm nnn
dmm c
dmf 7000
temp 22.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
N
O
BocHN
N
Cl
49
9
8
7
6
5
4
3
2
1
0 ppm
0.75
0.85
0.71
0.85
0.80
0.94
0.90
2.59
1.13
1.00
8.87

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 9 2012	dfrq	499.613
solvent	DMSO	dn	H1
file	/export/home/~	dpwr	34
	ds4/vnmrsys/data/i~	dof	0
	500/schreiber/shee~	dm	nnn
	han/PTS-901.fid	dmm	c
ACQUISITION		dmf	8412
sfrq	499.614	dseq	
tn	H1	dres	1.0
at	2.048	homo	n
np	32768	temp	23.0
sw	8000.0	PROCESSING	
fb	4000	lb	0.10
bs	8	wtfile	
ss	2	proc	ft
tpwr	54	fn	not used
pw	6.0	math	f
d1	0.300		
tof	500.0	werr	
nt	32	wexp	
ct	32	wbs	
alock	n	wnt	wft
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	5995.1		
vs	21		
sc	0		
wc	250		
hzmm	23.98		
is	70.99		
rfl	2250.5		
rfp	1269.0		
th	1		
ins	3.000		
ai ph			



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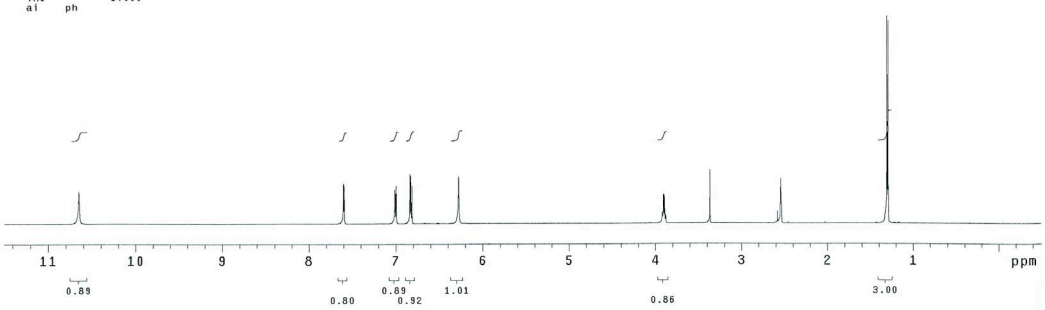
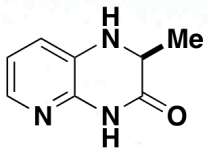


STANDARD CARBON PARAMETERS

exp3 s2pul

SAMPLE		DEC. & VT	
date	Feb 29 2012	dfrq	499.877
solvent	DMSO	dn	H1
file	/export/home/~	dpwr	48
	i500c/vnmrsys/data~	dof	0
	/schreiber/sheehan~	dm	yyy
	/PTS-504-C13.fid	dmm	w
ACQUISITION		dmf	8264
sfrq	125.707	dseq	
tn	C13	dres	1.0
at	1.092	homo	n
np	65536	temp	25.0
sw	29996.3	DEC2	
fb	not used	dfrq2	0
bs	32	dn2	
tpwr	55	dpwr2	1
pw	5.8	dof2	0
d1	0	dm2	n
tof	2000.0	dmm2	c
nt	9999	dmf2	10000
ct	1239	dseq2	
alock	n	dres2	1.0
gain	not used	homo2	n
FLAGS		DEC3	
il	n	dfrq3	0
in	n	dn3	
dp	y	dpwr3	1
hs	nn	dof3	0
DISPLAY		dm3	n
sp	-1147.3	dmm3	c
wp	29995.3	dmf3	10000
vs	91	dseq3	
sc	0	dres3	1.0
wc	250	homo3	n
hzmm	119.98	PROCESSING	
is	500.00	lb	1.00
rfl	6113.1	wtfile	
rfp	4964.9	proc	ft
th	7	fn	not used
ins	100.000	math	f
nm cdc ph			
		werr	
		wexp	
		wbs	
		wnt	



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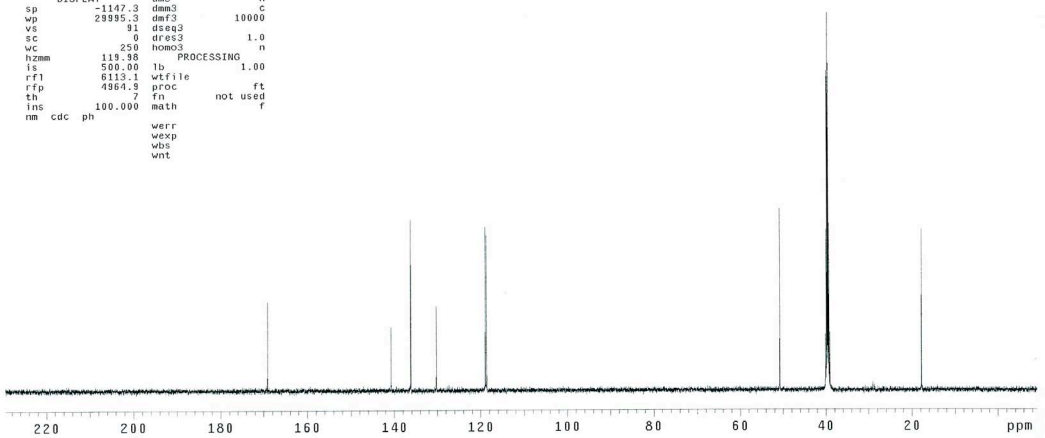
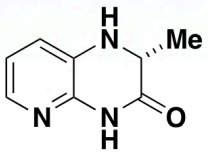


STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 29 2012	dfrq	499.613
solvent	DMSO	dn	H1
file	/export/home/~	dpwr	34
	ds4/vnmrsys/data/i~	dof	0
	500/schreiber/shee~	dm	nnn
	han/PTS-WYK-17102.~	dmm	c
	fid	dmf	8412
ACQUISITION		dseq	
sfrq	499.614	dres	1.0
tn	H1	homo	n
at	2.048	temp	23.0
np	32768	PROCESSING	
sw	8000.0	lb	0.10
fb	4000	wtfile	
bs	8	proc	ft
ss	2	fn	not used
tpwr	54	math	f
pw	6.0		
d1	0.300	werr	
tof	500.0	wexp	
nt	32	wbs	
ct	0	wnt	wft
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.0		
wp	5995.1		
vs	23		
sc	0		
wc	250		
hzmm	23.98		
is	92.14		
rfl	2250.5		
rfp	1269.0		
th	1		
ins	3.000		
ai ph			



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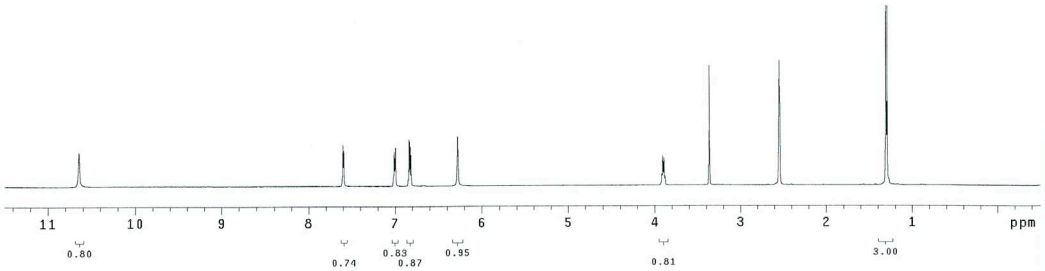
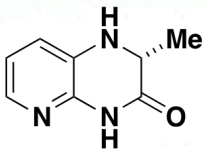


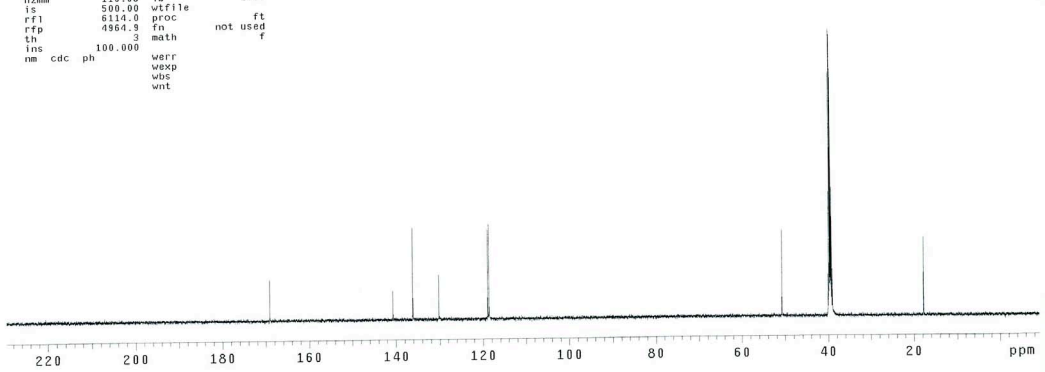
STANDARD CARBON PARAMETERS

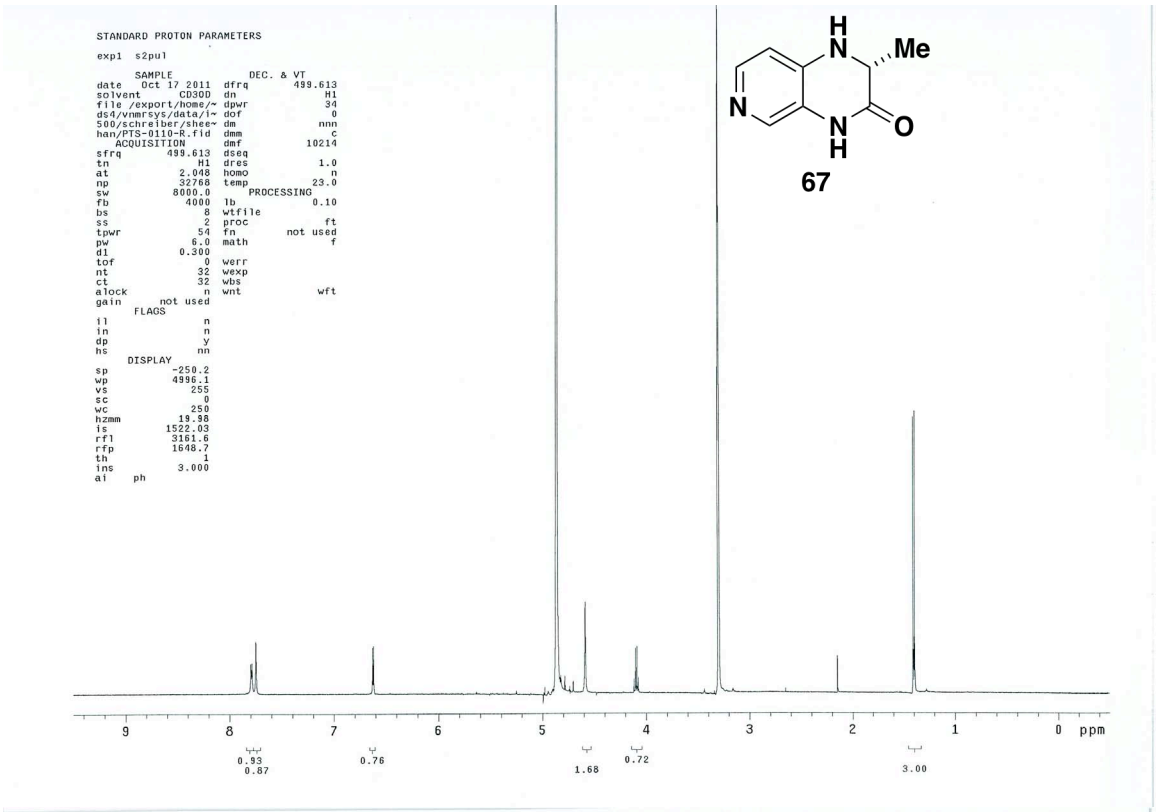
exp3 s2pul

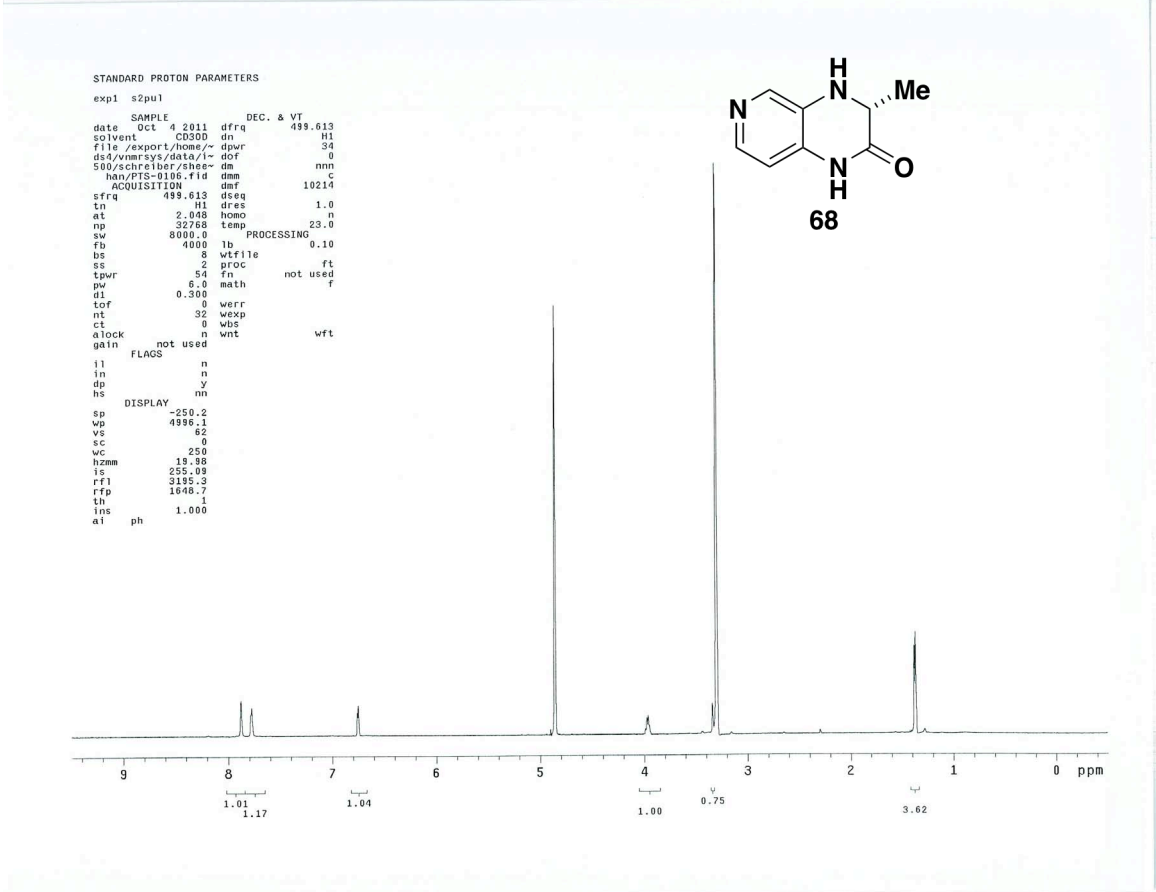
SAMPLE		DEC. & VT	
date	Feb 29 2012	dfrq	499.877
solvent	DMSO	dn	H1
file	/export/home/~	dpwr	48
	i500c/vnmrsys/data~	dof	0
	/schreiber/sheehan~	dm	yyy
	/PTS-WYK-17102-C13~	dmm	w
	.fid	dmf	8264
ACQUISITION		dseq	
sfrq	125.707	dres	1.0
tn	C13	homo	n
at	1.092	temp	25.0
np	65536	DEC2	
sw	29996.3	dfrq2	0
fb	not used	dn2	
bs	32	dpwr2	1
tpwr	55	dof2	0
pw	5.8	dm2	n
d1	0	dmm2	c
tof	2000.0	dmf2	10000
nt	9999	dseq2	
ct	1392	dres2	1.0
alock	n	homo2	n
gain	not used	DEC3	
FLAGS		dfrq3	0
il	n	dn3	
in	n	dpwr3	1
dp	y	dof3	0
hs	nn	dm3	n
DISPLAY		dmm3	c
sp	-1148.2	dmf3	10000
wp	29995.3	dseq3	
vs	69	dres3	1.0
sc	0	homo3	n
wc	250	PROCESSING	
hzmm	119.98	lb	1.00
is	500.00	wtfile	
rfl	6114.0	proc	ft
rfp	4964.9	fn	not used
th	3	math	f
ins	100.000		
nm cdc ph		werr	
		wexp	
		wbs	
		wnt	

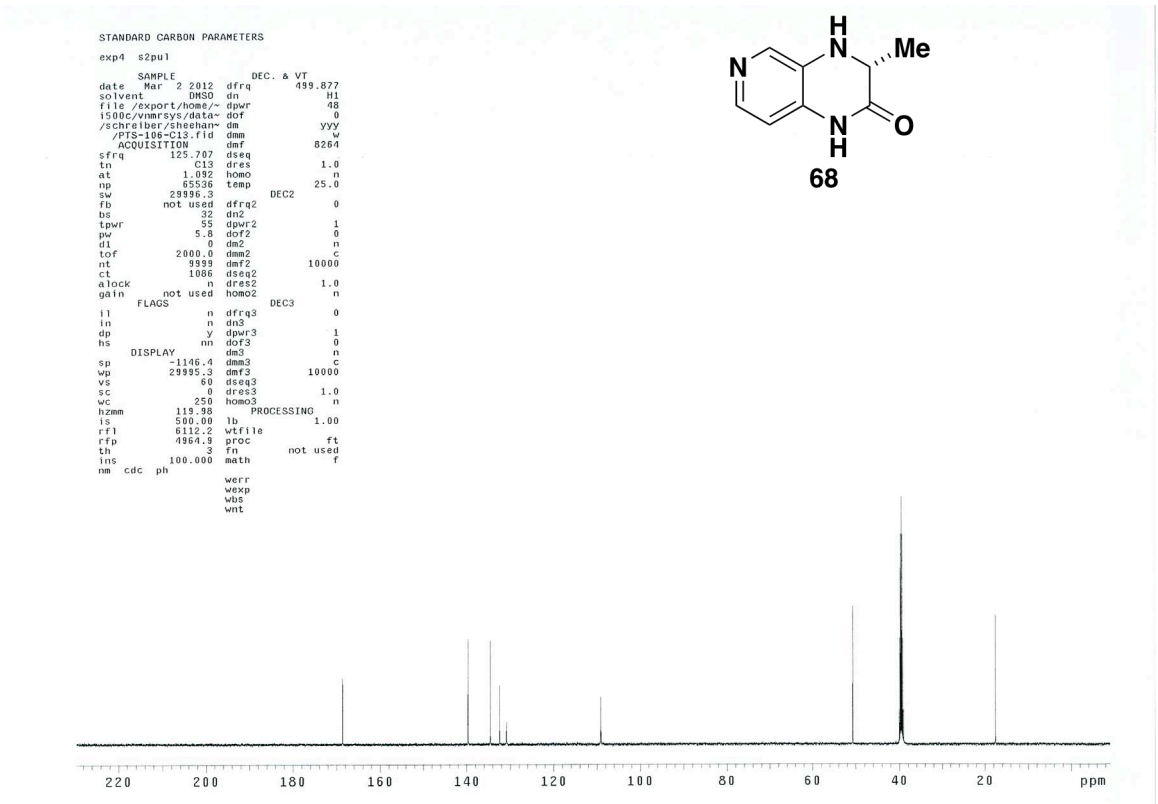


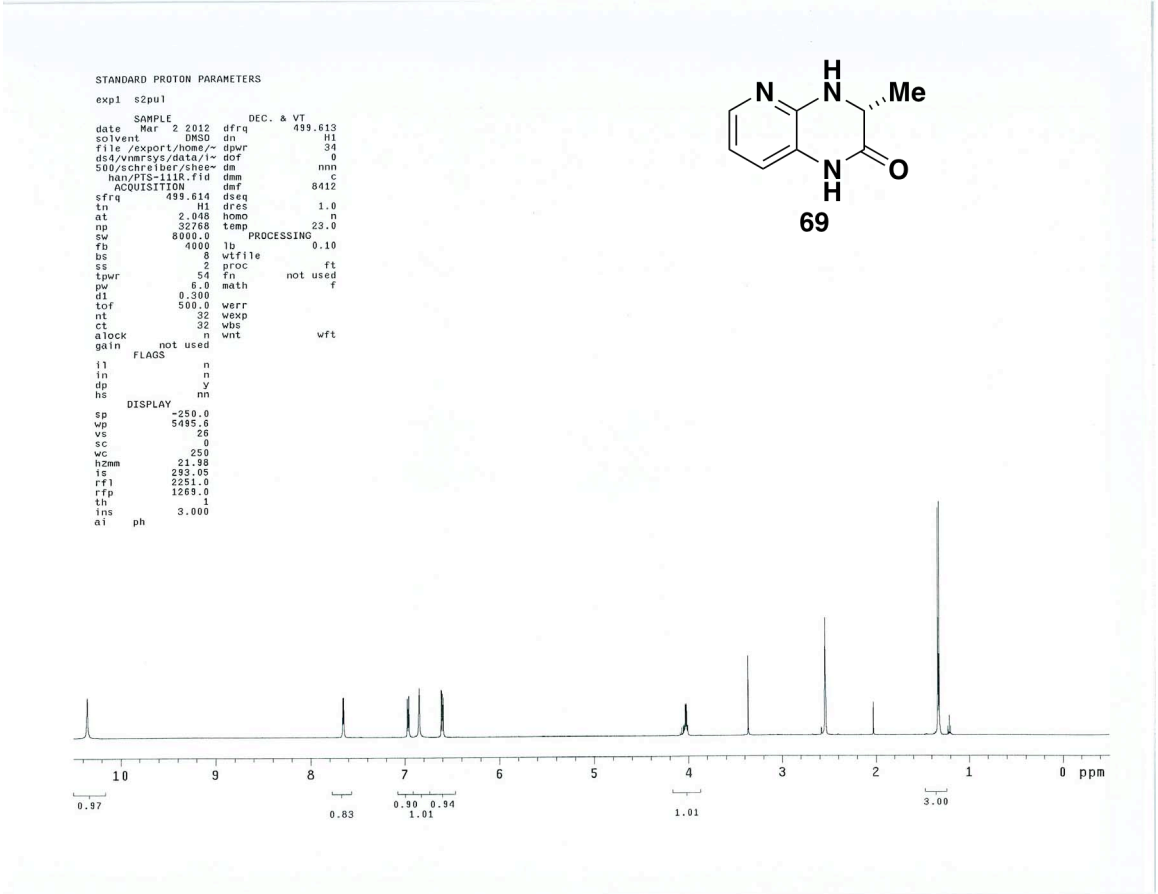
66

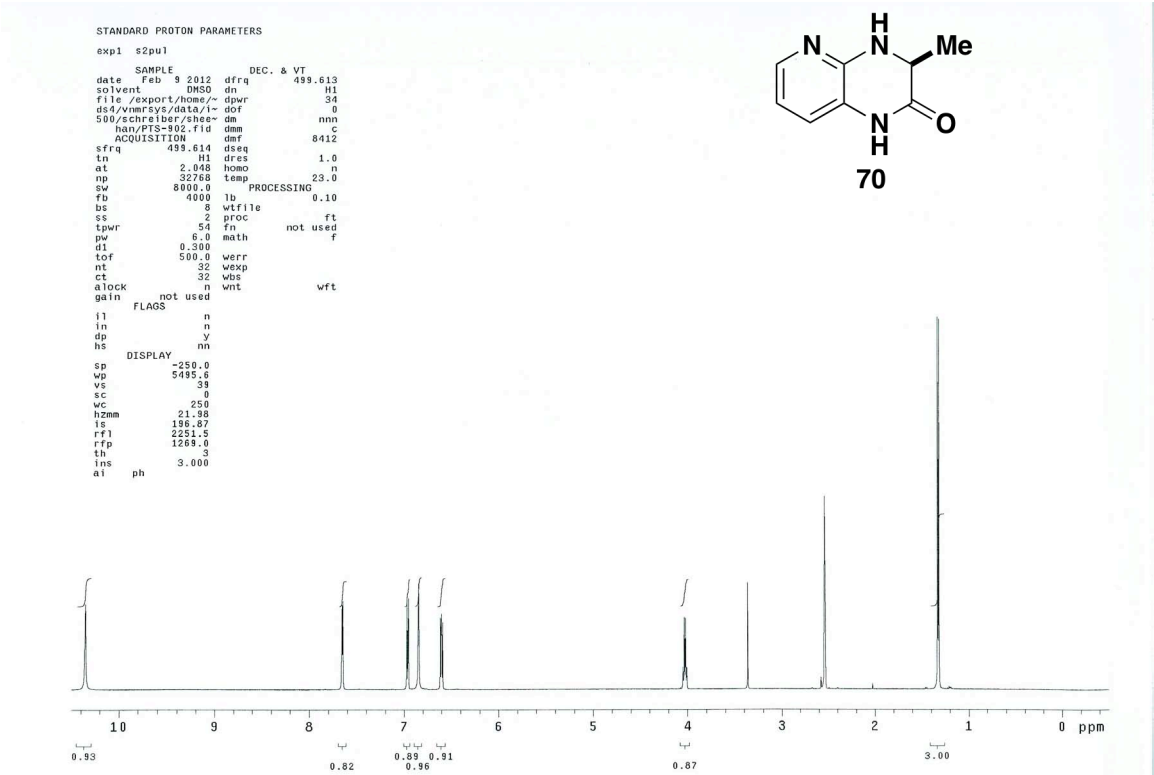


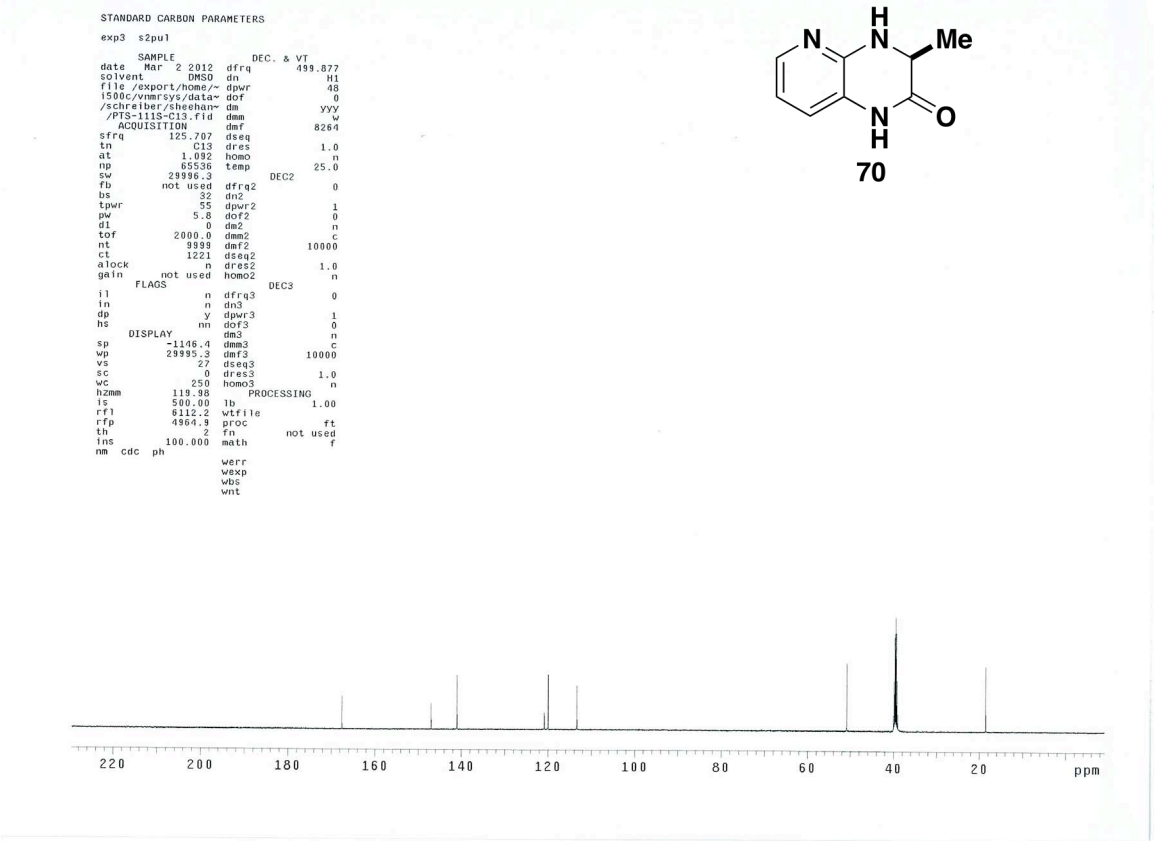

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Oct 17 2011
solvent CD3OD
file /export/home/~
ds4/vnmrsys/data/i~
500/schreiber/shee~
han/PTS-0110-R.fid
ACQUISITION
sfrq 499.613
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 8
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4996.1
vs 255
sc 0
wc 250
hzmm 19.98
is 1522.03
rfl 3161.6
rfp 1648.7
th 1
ins 3.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 10214
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
67
9 8 7 6 5 4 3 2 1 0 ppm
0.93
0.87
0.76
1.68
0.72
3.00

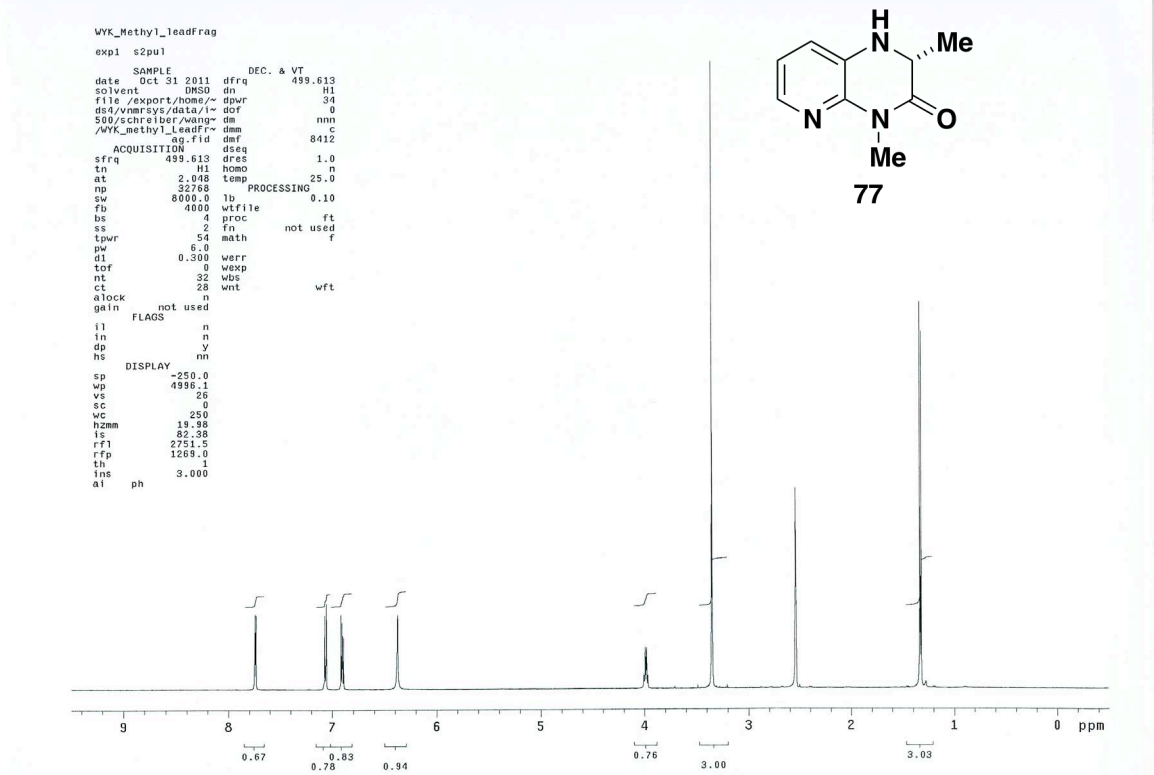

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Oct 4 2011
solvent CD3OD
file /export/home/~
ds4/vnmrsys/data/i~
500/schreiber/shee~
han/PTS-0106.fid
ACQUISITION
sfrq 499.613
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 8
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 0
nt 32
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4996.1
vs 62
sc 0
wc 250
hzmm 19.98
is 255.09
rfl 3195.3
rfp 1648.7
th 1
ins 1.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 10214
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
68
9 8 7 6 5 4 3 2 1 0 ppm
1.01
1.17
1.04
1.00
0.75
3.62

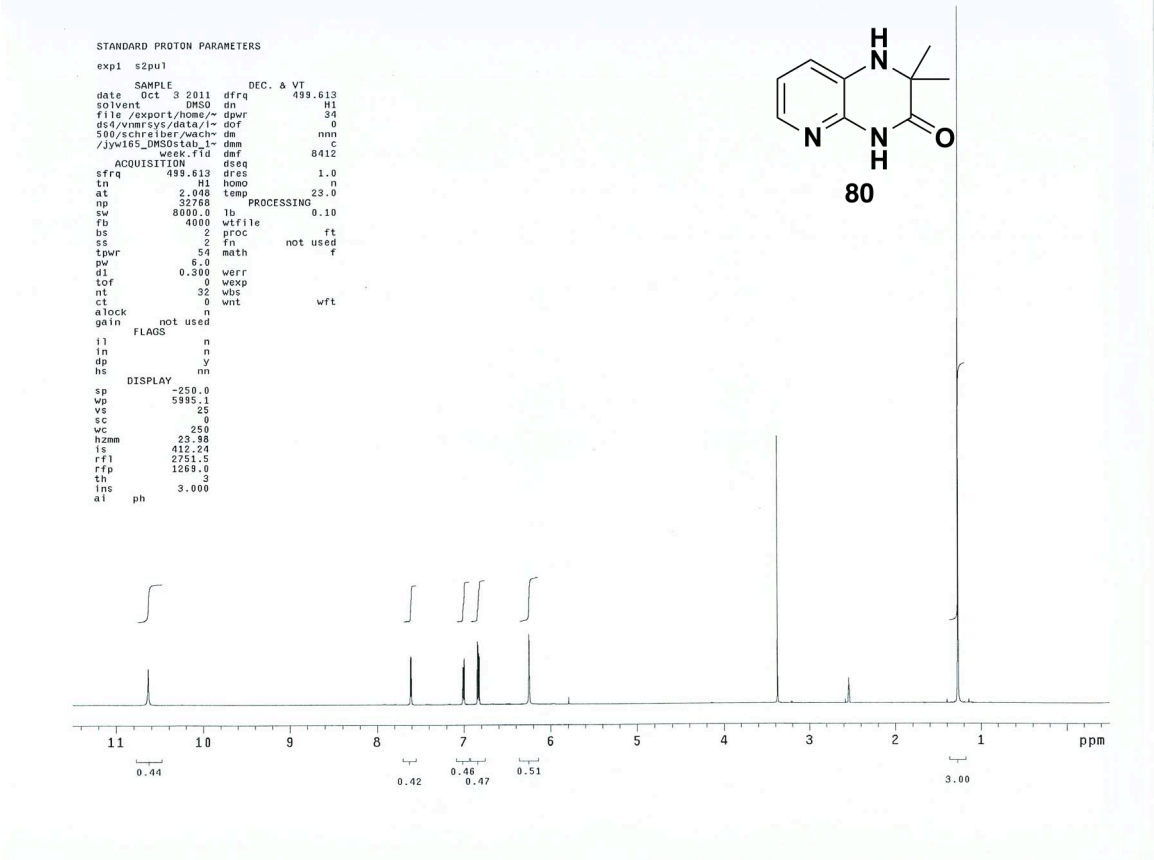

STANDARD CARBON PARAMETERS
exp4 s2pul
SAMPLE
date Mar 2 2012
solvent DMSO
file /export/home/~
i500c/vnmrsys/data~
/schreiber/sheehan~
/PTS-106-C13.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 5.8
d1 0
tof 2000.0
nt 9999
ct 1086
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1146.4
wp 29995.3
vs 60
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 6112.2
rfp 4964.9
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.877
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8264
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
H
N
Me
N
O
N
H
68
220
200
180
160
140
120
100
80
60
40
20
ppm

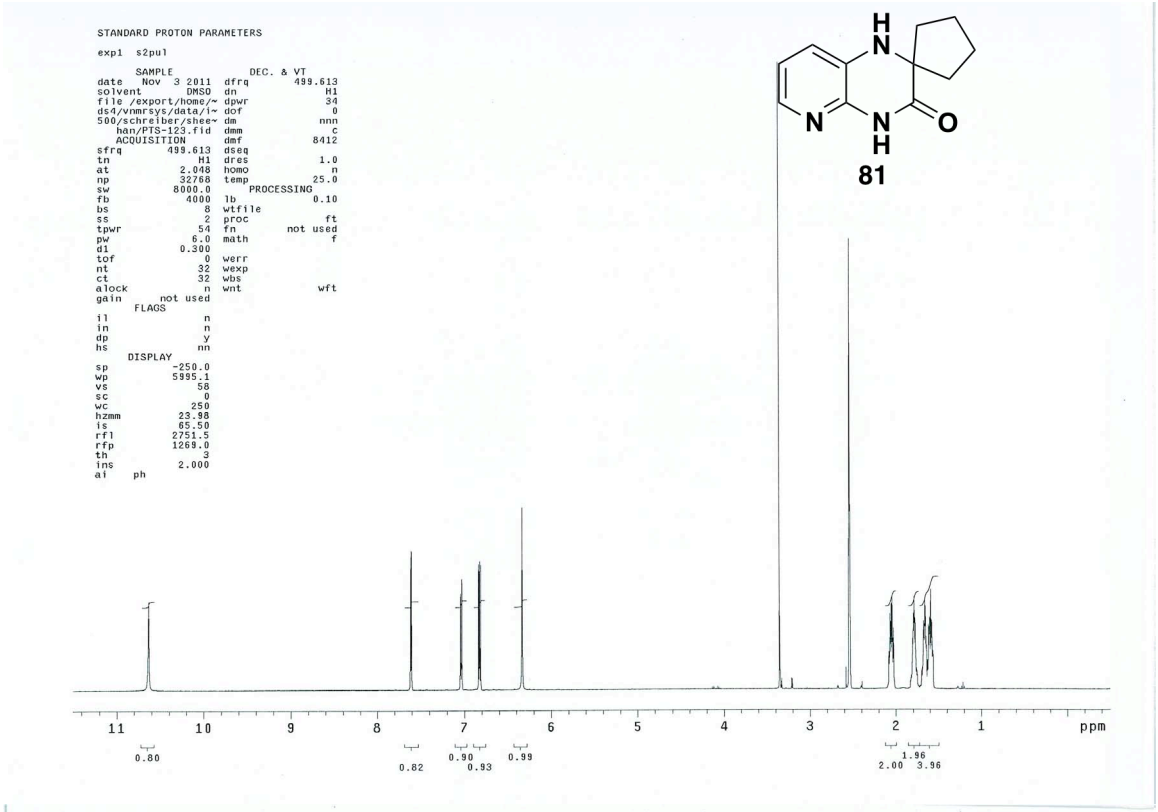

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Mar 2 2012
solvent DMSO
file /export/home/~
ds4/vnmrsys/data/i~
500/schreiber/shee~
han/PTS-11R.fid
ACQUISITION
sfrq 499.614
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 8
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 500.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5495.6
vs 26
sc 0
wc 250
hzmm 21.98
is 293.05
rfl 2251.0
rfp 1269.0
th 1
ins 3.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 8412
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
H
N
Me
N
O
N
H
69
10
9
8
7
6
5
4
3
2
1
0 ppm
0.97
0.83
0.90 0.94
1.01
1.01
3.00

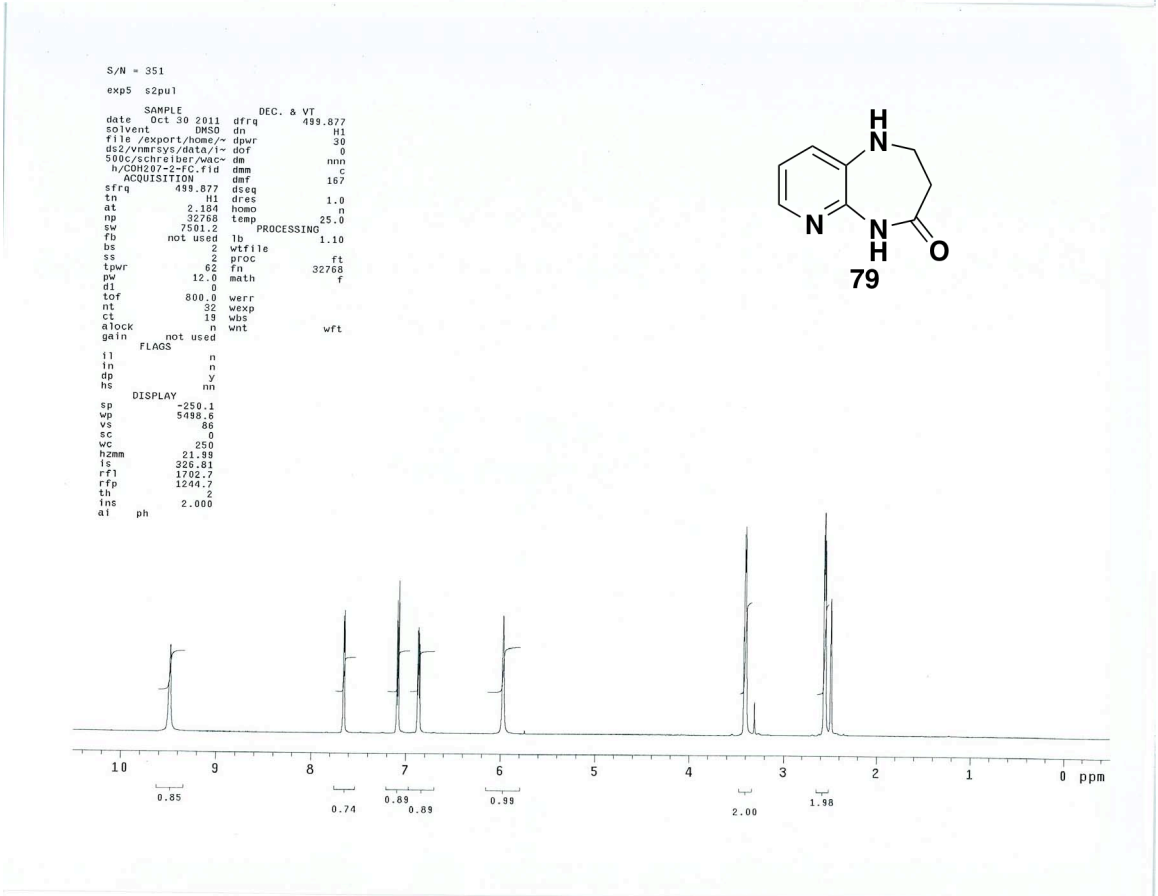

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Feb 9 2012
solvent DMSO
file /export/home/~
ds4/vnmrsys/data/i~
500/schreiber/shee~
han/PTS-902.fid
ACQUISITION
sfrq 499.614
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 8
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 500.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5495.6
vs 39
sc 0
wc 250
hzmm 21.98
is 196.87
rfl 2251.5
rfp 1269.0
th 3
ins 3.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 8412
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
H
N
N
Me
N
H
O
70
10
9
8
7
6
5
4
3
2
1
0 ppm
0.93
0.82
0.89
0.91
0.96
0.87
3.00

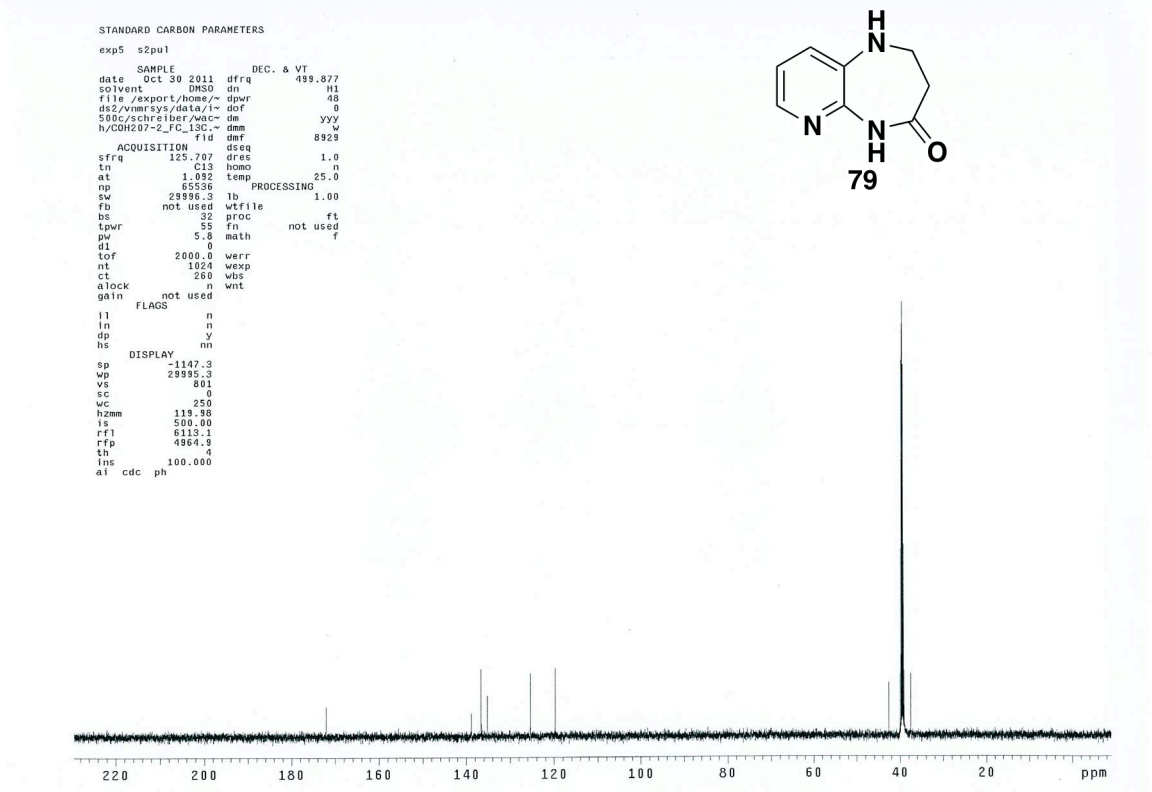

STANDARD CARBON PARAMETERS
exp3 s2pul
SAMPLE
date Mar 2 2012
solvent DMSO
file /export/home/~
i500c/vnmrsys/data~
/schreiber/sheehan~
/PTS-111S-C13.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 5.8
d1 0
tof 2000.0
nt 9999
ct 1221
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1146.4
wp 29995.3
vs 27
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 6112.2
rfp 4964.9
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.877
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8264
dseq
dres 1.0
homo n
temp 25.0
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 10000
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 10000
dseq3
dres3 1.0
homo3 n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
H
N
N
Me
N
H
O
70
220
200
180
160
140
120
100
80
60
40
20
ppm

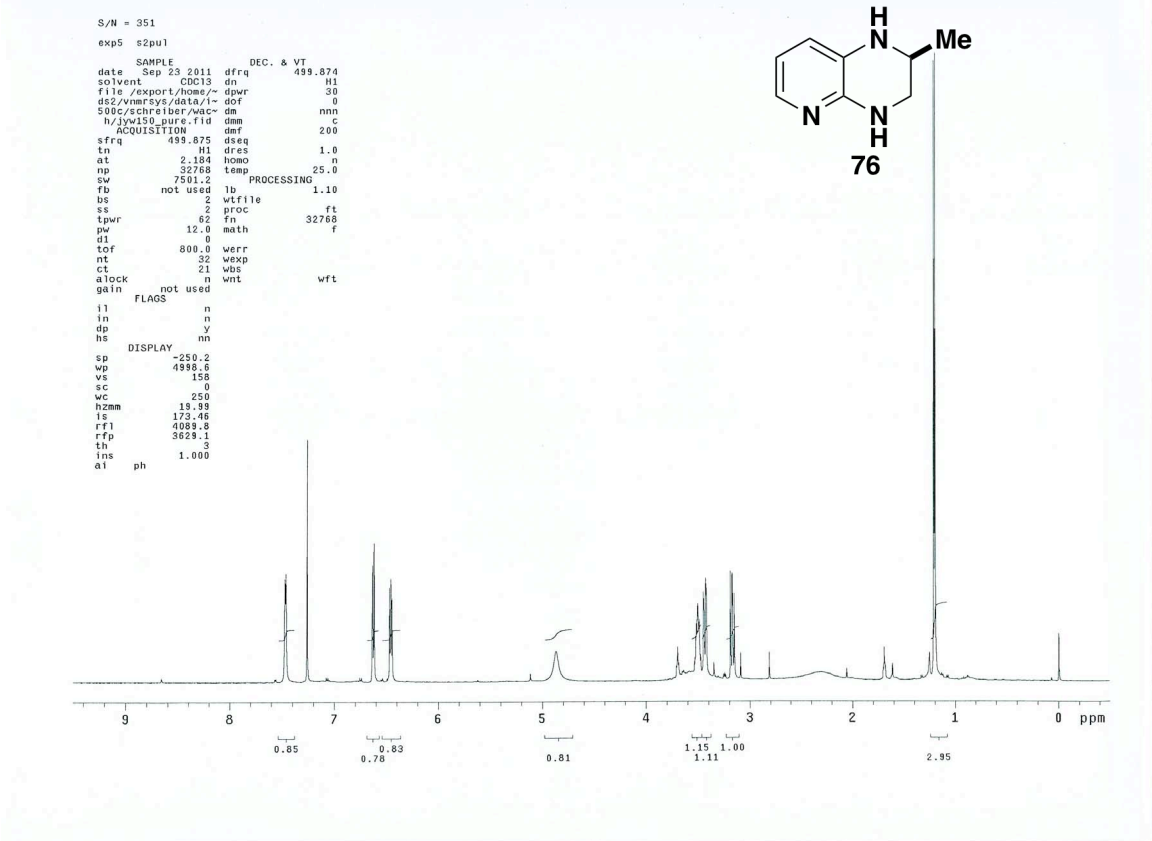

WYK_Methyl_leadFrag
exp1 s2pul
SAMPLE
date Oct 31 2011
solvent DMSO
file /export/home/~
ds4/vnmrsys/data/i~
500/schreiber/wang~
/WYK_methyl_Leadfr~
aq.fid
ACQUISITION
sfrq 499.613
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 0
nt 32
ct 28
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 4996.1
vs 26
sc 0
wc 250
hzmm 19.98
is 82.38
rfl 2751.5
rfp 1269.0
th 1
ins 3.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 8412
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
H
N
Me
N
N
O
Me
77
9
8
7
6
5
4
3
2
1
0 ppm
0.67
0.83
0.78
0.94
0.76
3.00
3.03

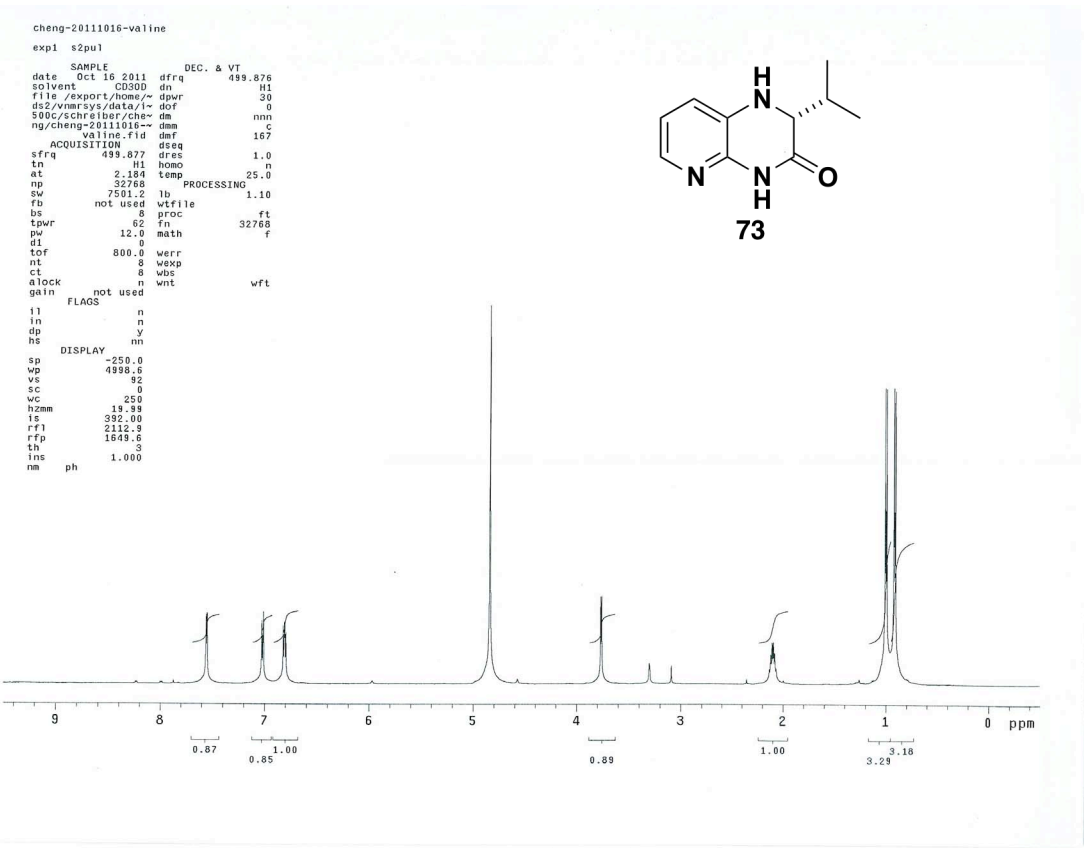

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Oct 3 2011
solvent DMSO
file /export/home/~
ds4/vnmrsys/data/i~
500/schreiber/wach~
/jyw165_DMSOstab_1~
week.fid
ACQUISITION
sfrq 499.613
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 2
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 0
nt 32
ct 0
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5995.1
vs 25
sc 0
wc 250
hzmm 23.98
is 412.24
rfl 2751.5
rfp 1269.0
th 3
ins 3.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 8412
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
H
N
N
O
H
80
11
10
9
8
7
6
5
4
3
2
1
ppm
0.44
0.42
0.46
0.47
0.51
3.00

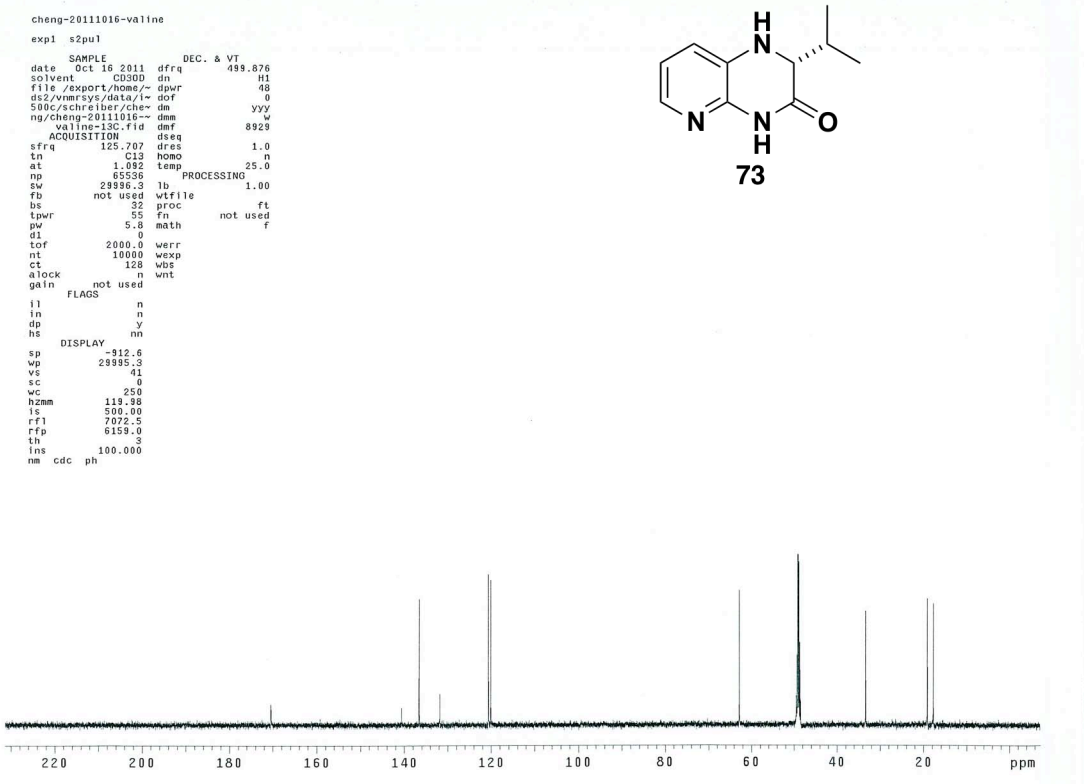

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Nov 3 2011
solvent DMSO
file /export/home/~
ds4/vnmrsys/data/i~
500/schreiber/shee~
han/PTS-123.fid
ACQUISITION
sfrq 499.613
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 8
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5995.1
vs 58
sc 0
wc 250
hzmm 23.98
is 65.50
rfl 2751.5
rfp 1269.0
th 3
ins 2.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 8412
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
H
N
N
H
O
81
11
10
9
8
7
6
5
4
3
2
1
ppm
0.80
0.82
0.90
0.93
0.99
1.96
2.00
3.96

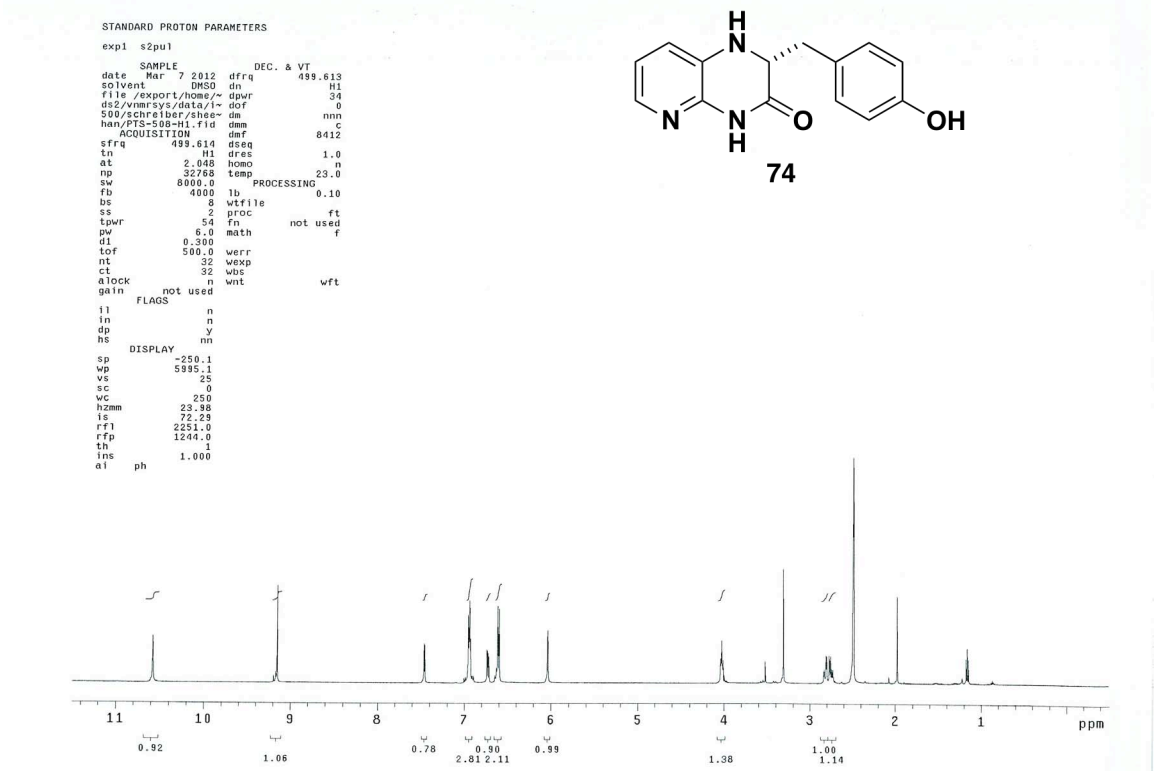

S/N = 351
exp5 s2pul
SAMPLE
date Oct 30 2011
solvent DMSO
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/wac~
h/CDH207-2-FC.fid
ACQUISITION
sfrq 499.877
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 2
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 19
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5498.6
vs 86
sc 0
wc 250
hzmm 21.99
is 326.81
rfl 1702.7
rfp 1244.7
th 2
ins 2.000
ai ph
DEC. & VT
dfrq 499.877
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 167
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
H
N
N
H
O
79
10
9
8
7
6
5
4
3
2
1
0 ppm
0.85
0.74
0.89
0.89
0.99
2.00
1.98

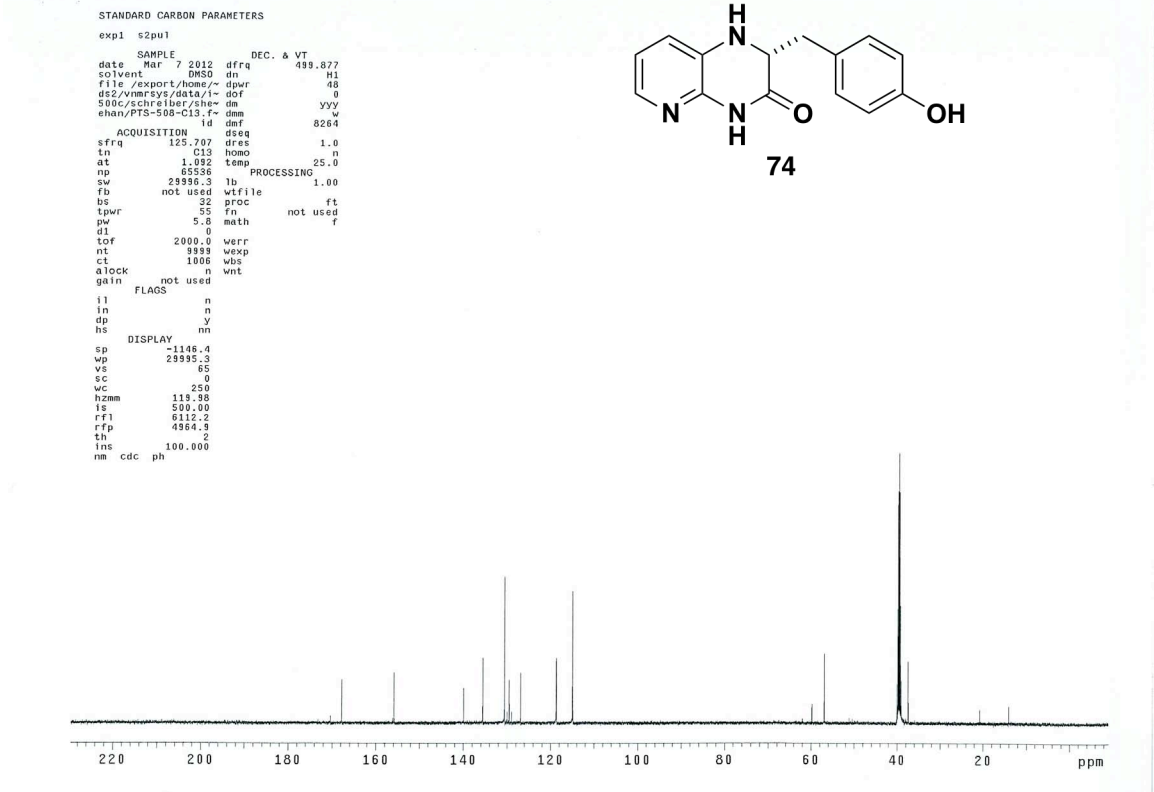

STANDARD CARBON PARAMETERS
exp5 s2pul
SAMPLE
date Oct 30 2011
solvent DMSO
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/wac~
h/COH207-2_FC_13C.~
fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 5.8
d1 0
tof 2000.0
nt 1024
ct 260
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1147.3
wp 29995.3
vs 801
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 6113.1
rfp 4964.9
th 4
ins 100.000
ai cdc ph
DEC. & VT
dfrq 499.877
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
H
N
N
H
N
O
79
220
200
180
160
140
120
100
80
60
40
20
ppm

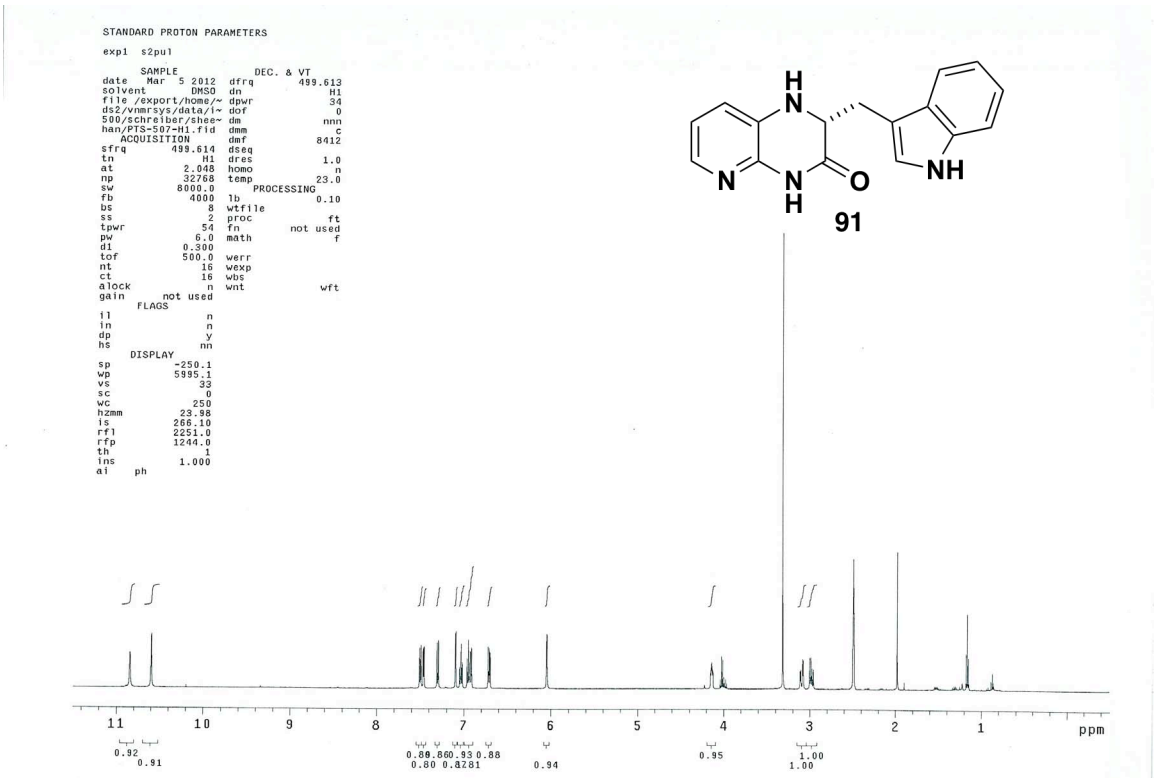

S/N = 351
exp5 s2pul
SAMPLE
date Sep 23 2011
solvent CDCl3
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/wac~
h/jyw150_pure.fid
ACQUISITION
sfrq 499.875
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 2
ss 2
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 32
ct 21
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.2
wp 4998.6
vs 158
sc 0
wc 250
hzmm 19.99
is 173.46
rfl 4089.8
rfp 3629.1
th 3
ins 1.000
ai ph
DEC. & VT
dfrq 499.874
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 200
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
H
N
Me
N
N
H
76
9
8
7
6
5
4
3
2
1
0
ppm
0.85
0.78
0.83
0.81
1.15
1.11
1.00
2.95

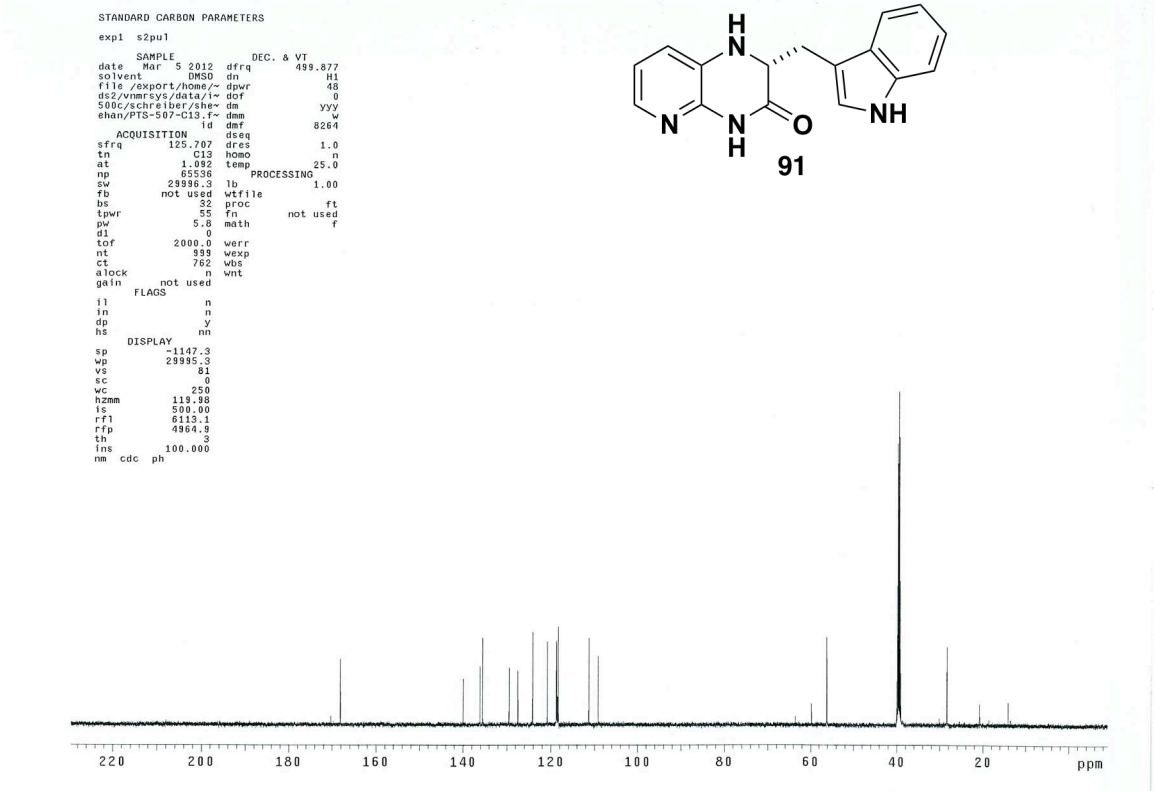

cheng-20111016-valine
exp1 s2pul
SAMPLE
date Oct 16 2011
solvent CD3OD
file /export/home/~
ds2/vnmrsys/data/l~
500c/schreiber/che~
ng/cheng-20111016~~
valine.fid
ACQUISITION
sfrq 499.877
tn H1
at 2.184
np 32768
sw 7501.2
fb not used
bs 8
tpwr 62
pw 12.0
d1 0
tof 800.0
nt 8
ct 8
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 4998.6
vs 92
sc 0
wc 250
hzmm 19.99
is 392.00
rfl 2112.9
rfp 1649.6
th 3
ins 1.000
nm ph
DEC. & VT
dfrq 499.876
dn H1
dpwr 30
dof 0
dm nnn
dmm c
dmf 167
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.10
wtfile
proc ft
fn 32768
math f
werr
wexp
wbs
wnt wft
H
N
N
N
H
O
73
9
8
7
6
5
4
3
2
1
0 ppm
0.87
1.00
0.85
0.89
1.00
3.18
3.29

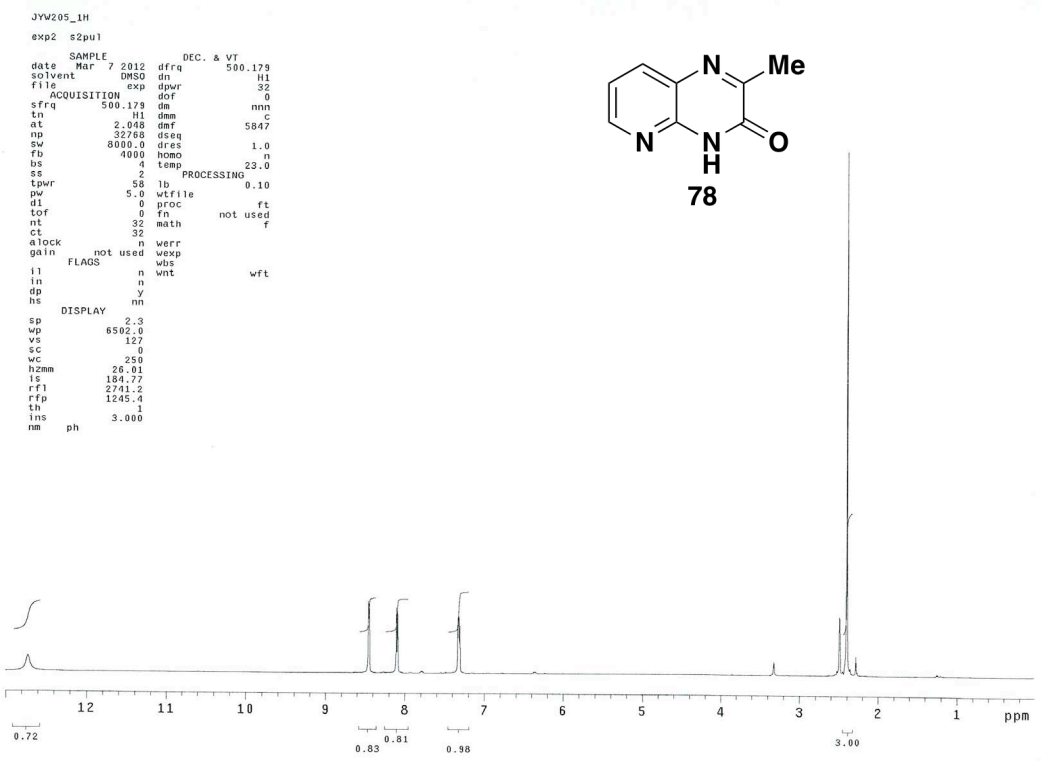

cheng-20111016-valine
exp1 s2pul
SAMPLE
date Oct 16 2011
solvent CD3OD
file /export/home/~
ds2/vnmrsys/data/l~
500c/schreiber/che~
ng/cheng-20111016~~
valine-13C.fid
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 5.8
d1 0
tof 2000.0
nt 10000
ct 128
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -912.6
wp 28995.3
vs 41
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 7072.5
rfp 6159.0
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.876
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8929
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
H
N
N
N
H
O
73
220
200
180
160
140
120
100
80
60
40
20
ppm

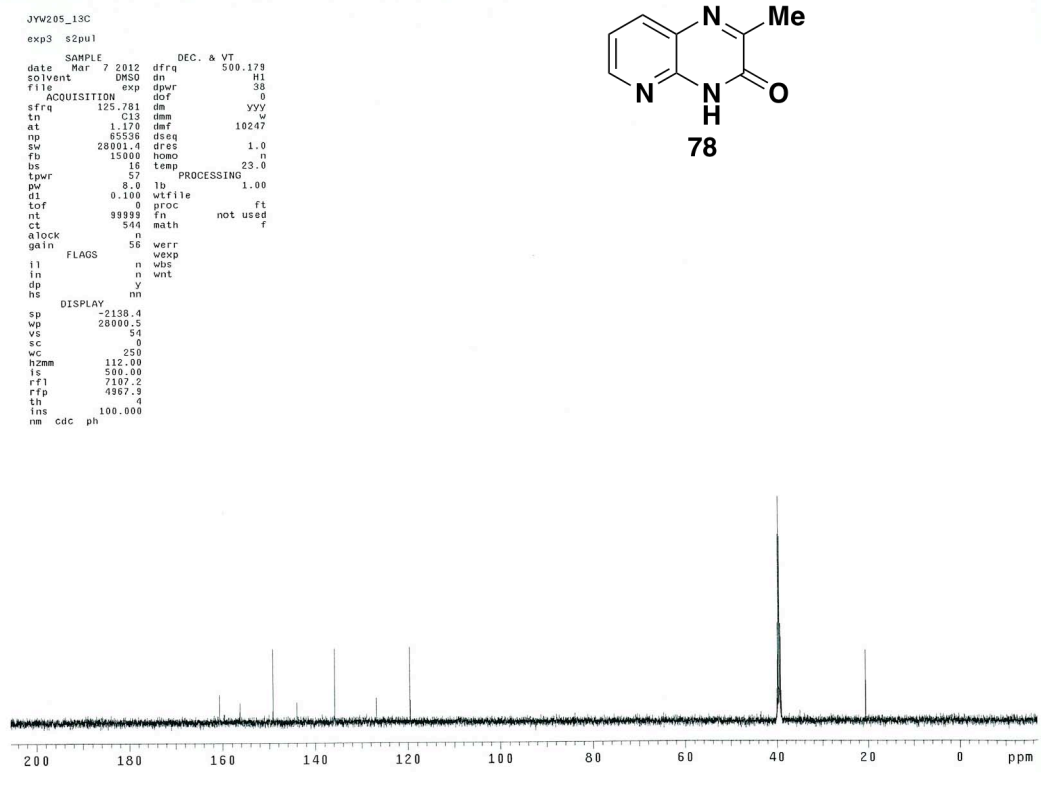

STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Mar 7 2012
solvent DMSO
file /export/home/~
ds2/vnmrsys/data/i~
500/schreiber/shee~
han/PTS-508-H1.fid
ACQUISITION
sfrq 499.614
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 8
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 500.0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5995.1
vs 25
sc 0
wc 250
hzmm 23.98
is 72.29
rfl 2251.0
rfp 1244.0
th 1
ins 1.000
al ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 8412
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
74
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
1.06
0.78
0.90
2.81 2.11
0.99
1.38
1.00
1.14


STANDARD CARBON PARAMETERS
exp1 s2pul
SAMPLE
date Mar 7 2012
solvent DMSO
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/she~
ehan/PTS-508-C13.f~
id
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 5.8
d1 0
tof 2000.0
nt 9999
ct 1006
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1146.4
wp 29995.3
vs 65
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 6112.2
rfp 4964.9
th 2
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.877
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8264
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
74
220
200
180
160
140
120
100
80
60
40
20
ppm


STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Mar 5 2012
solvent DMSO
file /export/home/~
ds2/vnmrsys/data/i~
500/schreiber/shee~
han/PTS-507-H1.fid
ACQUISITION
sfrq 499.614
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 8
ss 2
tpwr 54
pw 6.0
d1 0.300
tof 500.0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.1
wp 5995.1
vs 33
sc 0
wc 250
hzmm 23.98
is 266.10
rfl 2251.0
rfp 1244.0
th 1
ins 1.000
ai ph
DEC. & VT
dfrq 499.613
dn H1
dpwr 34
dof 0
dm nnn
dmm c
dmf 8412
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
91
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.91
0.80 0.86 0.93 0.88
0.80 0.87 1.00
0.94
0.95
1.00
1.00


STANDARD CARBON PARAMETERS
exp1 s2pul
SAMPLE
date Mar 5 2012
solvent DMSO
file /export/home/~
ds2/vnmrsys/data/i~
500c/schreiber/she~
ehan/PTS-507-C13.f~
id
ACQUISITION
sfrq 125.707
tn C13
at 1.092
np 65536
sw 29996.3
fb not used
bs 32
tpwr 55
pw 5.8
d1 0
tof 2000.0
nt 999
ct 762
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -1147.3
wp 29995.3
vs 81
sc 0
wc 250
hzmm 119.98
is 500.00
rfl 6113.1
rfp 4964.9
th 3
ins 100.000
nm cdc ph
DEC. & VT
dfrq 499.877
dn H1
dpwr 48
dof 0
dm yyy
dmm w
dmf 8264
dseq
dres 1.0
homo n
temp 25.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
91
220
200
180
160
140
120
100
80
60
40
20
ppm


JYW205_1H
exp2 s2pul
SAMPLE
date Mar 7 2012
solvent DMSO
file exp
ACQUISITION
sfrq 500.179
tn H1
at 2.048
np 32768
sw 8000.0
fb 4000
bs 4
ss 2
tpwr 58
pw 5.0
d1 0
tof 0
nt 32
ct 32
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp 2.3
wp 6502.0
vs 127
sc 0
wc 250
hzmm 26.01
is 184.77
rfl 2741.2
rfp 1245.4
th 1
ins 3.000
nm ph
DEC. & VT
dfrq 500.179
dn H1
dpwr 32
dof 0
dm nnn
dmm c
dmf 5847
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 0.10
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt wft
N
Me
N
N
H
O
78
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.72
0.83
0.81
0.98
3.00


JYW205_13C
exp3 s2pul
SAMPLE
date Mar 7 2012
solvent DMSO
file exp
ACQUISITION
sfrq 125.781
tn C13
at 1.170
np 65536
sw 28001.4
fb 15000
bs 16
tpwr 57
pw 8.0
d1 0.100
tof 0
nt 99999
ct 544
alock n
gain 56
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -2138.4
wp 28000.5
vs 54
sc 0
wc 250
hzmm 112.00
is 500.00
rfl 7107.2
rfp 4967.9
th 4
ins 100.000
nm cdc ph
DEC. & VT
dfrq 500.179
dn H1
dpwr 38
dof 0
dm yyy
dmm w
dmf 10247
dseq
dres 1.0
homo n
temp 23.0
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
N
Me
N
N
H
O
78
200
180
160
140
120
100
80
60
40
20
0
ppm